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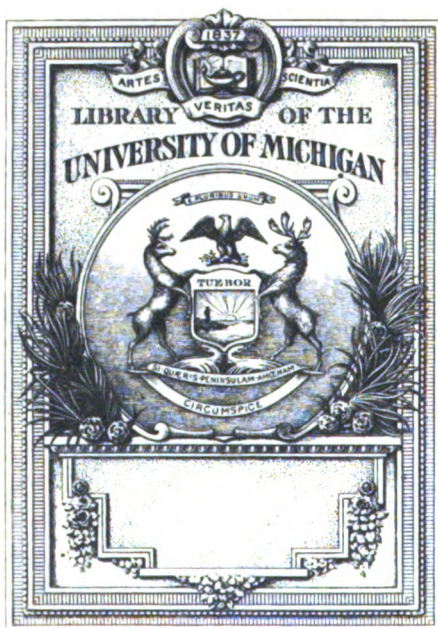
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JOURNAL OF SCIENCE.

CONDUCTED BY

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SIR JOSEPH JOHN THOMSON, O.M., M.A., Sc.D., LL.D., F.R.S.  
JOHN JOLY, M.A., D.Sc., F.R.S., F.G.S.  
RICHARD TAUNTON FRANCIS

AND

WILLIAM FRANCIS, F.L.S.

---

"Nec araneorum sane textus ideo melior quia ex se fila gignunt, nec noster  
vilior quia ex alienis libamus ut apes." JUST. LIPS. *Polit. lib. i. cap. i. Not.*

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VOL. XLVI.—SIXTH SERIES.

JULY—DECEMBER 1923.

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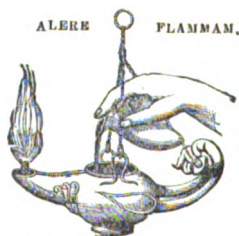
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perspicua .... Admiratio generat quaestionem, quaestio investigationem,  
investigatio inventionem.”—*Hugo de S. Victore.*

—“Cur spirent venti, cur terra dehiscat,  
Cur mare turgescat, pelago cur tantus amaror,  
Cur caput obscura Phœbus ferrugine condant,  
Quid toties diros cogat flagrare cometas,  
Quid pariat nubes, veniant cur fulmina cœlo,  
Quo micet igne Iris, superos quis conciat orbes  
Tam vario motu.”

*J. B. Pinelli ad Mazonium.*



*Published the First Day of every Month.*

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THE  
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PHILOSOPHICAL MAGAZINE,  
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JOURNAL OF SCIENCE.

*Being a Continuation of Tilloch's 'Philosophical Magazine,'  
Nicholson's 'Journal,' and Thomson's 'Annals of Philosophy.'*

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**SIXTH SERIES.**

**N° 271.—JULY 1923.**

**WITH THREE PLATES.**

Illustrative of Prof. F. H. NEWMAN's Paper on the Absorption produced by Electrically Luminescent Sodium Vapour; Mr. B. E. MOURASHKINSKY's on Diffraction Pattern in a case of two very close Point-Light Sources; and Mr. SATYENDRA RAY's on Images obtained by means of a Semi-infinite Obstacle.

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[SIXTH SERIES.]

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JULY 1923.

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- I. *The Theory of Mensuration.* By DOROTHY WRINCH, D.Sc., Fellow of Girton College, Cambridge, and Member of the Research Staff, University College, London, and HAROLD JEFFREYS, M.A., D.Sc., Fellow of St. John's College, Cambridge\*.

PART I.—PRELIMINARY CONSIDERATIONS.

*The Nature of Laws and Individual Experience.*

THE interest of science rests principally in its laws, and not in its data. Particular sensations have interest for science only in so far as they make it possible to discover and verify laws; the experiencing of a sensation, apart from the conditions that accompany it, affords no basis for an inference, and must remain permanently part of the unsystematized data not included in science. The data that can be utilized are simultaneous occurrences of two or more sensations, not the individual sensations themselves; they are therefore instances of relations between sensations. The discovery of a law consists in finding a relation that is common to a considerable number of data. From such a relation, given that a certain set of sensations (which we shall call the circumstances) occurs, it is possible to infer that another sensation determined by the relation must also occur.

\* Communicated by the Authors.

*Phil. Mag. S. 6. Vol. 46. No. 271. July 1923.*

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It is thus of fundamental importance to notice the difference in structure between a law and a proposition embodying the result of a single observation. We may denote a law, a proposition that a certain relation between circumstances  $k$  and sensations  $a$  will always be found to hold\*, however  $k$  and  $a$  themselves may vary, by  $(m)f(a_m, k_m)$ . A particular datum or consequence of the law may then be denoted by  $f(a_s, k_s)$ . The interest for science of the fact that a certain investigator at a certain moment at a certain place had a certain set of sensations exists only in the possibility that it offers of affording an instance of a general proposition relating such sets of sensations.

The above notation draws attention to the fact that there is no essential structural difference between a law  $(m)f(a_m, k_m)$  that is capable of verification, and one  $(m)f(b_m, l_m)$  that is incapable of verification. In the one case it is asserted that a sensation  $a$  will be experienced under conditions that can in point of fact on occasion be satisfied. In the other case it is asserted that a sensation  $b$  will be experienced, given that certain conditions are satisfied, the conditions being such that they cannot in fact be satisfied. But there is no difference between the forms of the relations between the sensations and the circumstances in the two cases. In the case of Einstein's theory of gravitation, for instance, the tests of the motion of the perihelion of Mercury and the bending of a ray of light are instances of the first type of law; while it appears probable that the law of the shift of the lines in the solar spectrum could be tested only in circumstances that cannot, in fact, be realised.

There is no methodological difference between the data obtained by experiment and observation. In each case an association of sensations is recorded, and laws are inferred purely from such associations. The difference between experiment and observation is that in the latter the combination of circumstances  $k_m$  is not subject to the control of the investigator, who merely notes the occurrence of  $a_m$  at the instant when his changing sensations include  $k_m$ ; whereas in an experiment the investigator brings about the conditions  $k_m$  himself. Usually  $k_m$  depends only partly on the experimenter's actions. Perhaps an experiment on cathode rays represents the extreme of control that is possible; while extreme lack of control might be represented by eye observations, without a nephoscope, of the

\* The symbol  $(x)f(x)$  is habitually used in modern logic to denote the assertion that, for all values of  $x$ , the proposition  $f(x)$  is true.

direction of motion of clouds. Even in the latter case, however, action on the part of the observer is necessary to obtain any result: he must open his eyes and look at the sky. Most scientific observations, however, are intermediate in character. In astronomy, for instance, the motion of the heavenly body is independent of the observer, but the telescope must be entirely under his control for the results to be of any value. In every case, however, what matters is the fact that a certain sensation was experienced in conjunction with certain others; in the subsequent development one utilises this fact, and no further reference is made to the part played by the observer in bringing about the conditions necessary to make the observation possible.

In some cases, laws will differ only in that the circumstances  $k_m$  under which a certain sensation is asserted to be experienced are replaced by  $k_m'$ , where  $k_m'$  is more or less narrowly specified than  $k_m$ . In general, the specification of  $a$  will not be enough to determine the conditions of its occurrence, though the truth of a law asserts that the circumstances entail the occurrence of  $a$ .

At any one stage of scientific knowledge, the important question is whether certain consequences of the laws under consideration at the moment will be verified or not. In the case of a law with several verifiable consequences, some of which have already been verified, we have to assess the probabilities of certain other propositions, given these various pieces of information. We have, in fact, to deal with

$$P\{f(a_m, k_m) : f(a_1, k_1) \cdot f(a_2, k_2) \dots f(a_{m-1}, k_{m-1}) \cdot h\}$$

if we wish to discuss the probability that some further prediction will be verified, and with

$$P\{(m)f(a_m, k_m) : f(a_1, k_1) \dots f(a_s, k_s) \cdot h\}$$

if we are considering the probability of the law itself.

### *The Modified Simplicity Postulate.*

It is of vital importance for the understanding of the propositions of science that one should realize that the term  $k$  occurs in every proposition. Hence the simplicity postulate introduced in a previous paper requires a slight modification, since it evidently needs to be stated in a form that



makes the  $k$  term explicit. We therefore restate it in the following form :—

If  $(m)f_1(a_m, k_m), (m)f_2(a_m, k_m), \dots (m)f_n(a_m, k_m)$  are all general laws, concerning the truth of which for the admissible values of  $k$  we have no previous relevant information, the prior probabilities of these laws, namely

$$\begin{aligned} &P\{(m)f_1(a_m, k_m) : h\}, \\ &P\{(m)f_2(a_m, k_m) : h\} \dots P\{(m)f_s(a_m, k_m) : h\} \end{aligned}$$

are all finite, but constitute the terms of a convergent series, and accordingly are  $\aleph_0$  in number; further, the simpler the law, the higher its prior probability.

By the method of our former paper we have

$$\begin{aligned} &P\{f(a_1, k_1) \cdot f(a_2, k_2) \dots f(a_m, k_m) : h\} \\ &= P\{f(a_m, k_m) : f(a_1, k_1) \dots f(a_{m-1}, k_{m-1}) \cdot h\} \\ &\quad \times P\{f(a_1, k_1) \dots f(a_{m-1}, k_{m-1}) : h\} \\ &= P\{f(a_1, k_1) : h\} P\{f(a_2, k_2) : f(a_1, k_1) \cdot h\} \dots \\ &\quad \times P\{f(a_m, k_m) : f(a_1, k_1) \dots f(a_{m-1}, k_{m-1}) \cdot h\}. \end{aligned}$$

Our hypothesis requires that the quantity on the left shall be finite, and shall tend to a definite limit different from zero as  $m$  tends to infinity; for its limit is the probability of the general law  $P\{(m)f(a_m, k_m) : h\}$ . Hence, whatever number  $\lambda$  less than unity is selected, there cannot be more than a finite number of factors less than  $\lambda$  on the right. Hence, as  $m$  increases,

$$P\{f(a_m, k_m) : f(a_1, k_1) \dots f(a_{m-1}, k_{m-1}) \cdot h\}$$

must tend to unity as a limit. But  $f(a_m, k_m)$  is the proposition that  $a_m$  will be experienced if  $k_m$  occurs; and therefore it follows that the probability that the next verification will succeed if tried approaches to certainty as the number of verifications increases.

*Note.*—Prof. G. H. Hardy has called our attention to a slip in a previous paper (Phil. Mag. xlv. p. 370, 1923). A law involving a constant differing from an integer by  $\frac{1}{n}$ , where  $n$  is a large integer, would be expected to occupy a position in the probability series later than the  $m$ th, where

$$m = \sum_1^n \phi(n) = \Phi(n),$$

where  $\phi(n)$  is the number of numbers less than  $n$  and prime to it. The asymptotic value of  $\Phi(n)$  is  $\frac{3}{\pi^2} n^2 + O(n \log n)$ , given in Landau's *Primzahlen*, p. 579.

*The Verification of Intermediate Steps.*

The argument used in our former paper, concerning cases where the success of repeated verifications may make the law itself have a probability approaching certainty when the verifications are included among the relevant data, is still applicable when the constituent propositions are of the form  $f(a, k)$ . Consider now the law  $(m)f(a_m, k_m)$ , and its posterior probability based on several data of the form  $f(a_s, k_s)$ . These data may arise in two ways: first, they may be derived directly from experience; second, they may be inferences from laws already known. Considering the second possibility first, we notice that such inferences may themselves be laws of considerable generality; they may have probabilities approaching certainty, on account of the verifications of the laws they are derived from. When they are to be used in further inferences, it is quite unnecessary to verify them directly by experiment, for they are used only in the form "if  $k$  occurs,  $a$  will also occur"; and if this datum is practically certain from previous knowledge, it is a matter of complete indifference to its subsequent application whether it is verified directly. Indeed, it does not matter whether it is possible to verify it at all. Thus we arrive at the important general principle that the verification of intermediate steps is unnecessary. This will be used repeatedly in what follows; just as it has been used implicitly in every work on theoretical physics ever written.

In the case of a proposition  $f(a, k)$  derived directly from experience, we evidently do not require to insert as a separate datum in the probability estimate the fact that the circumstances  $k$  occurred, since this fact does not affect the probability of the propositions under consideration. For, first, if any  $k$  has not occurred, the corresponding  $a$  has not been verified as occurring with it, and therefore  $f(a, k)$  is not part of the available data relative to the law we are considering. Secondly, if it has occurred, it conveys no relevant information without the corresponding  $a$ , and therefore its mention except in its association with  $a$  is unnecessary.

*Judgments of Irrelevancy.*

The knowledge available with respect to any experiment or observation has reference to a very large number of circumstances. Thus, in the account of the experiment we may know the temperature of the laboratory, the time of day, the type of telescope used, and many other details.

The characterization will not be a complete account of the conditions of the experiment unless these details are exhaustively enumerated. In order to relate to a law a fact whose specification we have, it is customary to take into account only a few of them, and it is considered that the others are irrelevant to the purpose in hand.

It will be convenient to use  $k$  to denote only the aggregate of relevant circumstances, excluding from it the other circumstances involved. To say that the datum  $b$  is irrelevant is then to say that, for all values of  $b$ ,  $P\{(f(a, kb):k)\}$  is the same, provided that  $k$  remains unchanged. Thus to assert that  $b$  is irrelevant to a set of sensations is to say that the same sensations  $a$  occur with one value of  $b$  as with another. An assertion of irrelevance of this type is capable of direct test. For suppose a number of tests applied in which  $b$  has varying values, and that  $a$  is found to remain the same. There are two alternatives. First,  $a$  may really depend on both  $b$  and some other datum  $c$ , and the change in  $a$  dependent on the variation of  $b$  is just balanced by that due to the variation of  $c$ . This has an infinitesimal prior probability, since for every value of  $b$  it requires  $c$  to have a definite value; unless indeed  $b$  and  $c$  are themselves connected by a law, when the connexion can be observed and the law discovered, and it then ceases to be necessary to specify some part of  $bc$ . The alternative is to suppose that  $a$  is, in fact, independent of  $b$ . But independence is the simplest of all laws, and therefore always has a considerable prior probability. It corresponds to the simplest possible differential equation, namely

$$\frac{dy}{dx} = 0.$$

The two hypotheses, (1) that  $a$  and  $b$  are, in fact, independent, and (2) that the effect on  $a$  of variations in  $b$  is just annulled by unrelated variations in  $c$ , both imply the lack of experimental evidence for a connexion. The posterior probabilities, given that no connexion has been found between  $a$  and  $b$ , are therefore in the ratio of the prior probabilities, and therefore it is practically certain that  $a$  and  $b$  are independent. Thus the experimental establishment of independence is possible, and it is probable that independence is usually an empirical inference and not an *a priori* hypothesis. An electrical experiment is expected to give the same result independently of the time of day and the position of the laboratory, not because one has a prior belief that either

absolute or relative position and time are irrelevant, but because it was actually empirically proved that they are irrelevant in the course of the experiments that established the electrical law.

## PART II.—THE THEORY OF MENSURATION.

Mensuration may be defined as the science of the relations between measurements of distance in rigid bodies. It must be carefully distinguished from all forms of geometry, on account of the utter dissimilarity of the methods of development. The method of geometry is essentially intensive, while mensuration is essentially extensive, involving a principle of empirical generalization, like all other empirical sciences \*. Each geometry rests on a number of *a priori* general postulates. The development of any one geometry consists in the deduction of the consequences of any one set of mutually consistent postulates. In mensuration, on the other hand, we have to start with results obtained by actual experiment, which by their very nature have been tested for only a finite number of instances, and the results covering all cases, or indeed any other cases, arise only as generalizations in the course of the development, and not as part of the preliminary postulates.

It may be suggested that before a discussion of mensuration can be undertaken, the terms "distances," "rigid bodies," which are used in our specification of the subject-matter, should be defined. The reply to this requires a digression. In accordance with the principles enunciated in a former paper †, the main requirement of a definition is to make it possible to recognize the defined notion when it actually occurs. It is of no value to say that a rigid body is one such that the distances between all the points of it are unaltered by any displacement, nor to define relative motion as change of distance between parts of the system, unless we have some way of recognizing when distances *are* altered. Distance, again, cannot be defined in terms of the properties of rigid bodies unless we have first some method of recognizing the rigid body when we meet it. None of these notions can be defined in terms of the properties of space, because we have no means of recognizing space directly; distance in space, for instance, cannot be determined except through measurements, which at once re-introduce

\* For a fuller discussion of the distinction, see 'Nature,' Feb. 27, 1921, pp. 806-809.

† Phil. Mag. vol. xlii. pp. 369-390 (1921).

material scales, which the reference to space was intended to avoid.

The solution appears to be that none of these notions is directly recognizable, and that all are derived from still more elementary notions, several experimental facts being used in the process. Let us start from the notion of a body, without considering the processes by which we arrive at this. It is a fact that we can make permanent marks on bodies, which we can recognize afterwards. It is also a fact that two bodies can be made with "edges," so that when they touch at two parts of an edge they touch at all intermediate parts; also however they may be turned, subject to these two points remaining in contact, the intermediate parts all remain in contact. Given that this has been observed a sufficient number of times with one pair of bodies, we can use our principle of empirical generalization to infer with a high degree of probability that it will be the case in any subsequent trial with these bodies. In such cases we may call the edges "straight." The reservation must be made that the bodies must receive only ordinary treatment during the test. It is easy to recognize by our sensations of force when exceptional treatment is taking place. If edges fail to satisfy the test, they do not form part of the subject-matter of mensuration; and if edges that have been found to satisfy it in many previous trials fail in a new trial, we say that the conditions in the latter were exceptional. Thus experiment enables us to classify edges into (1) those straight and suitable for mensuration, and (2) those never straight or not permanently straight under ordinary conditions. The occurrence of failure in similar experiments on edges previously regarded as straight provides a standard of what conditions are to be regarded as exceptional. The same type of experiment therefore leads to standards both of straight edges and of ordinary conditions.

The straight edge may now be used to construct a definition of a rigid body. Marks may be made at intervals, quite arbitrarily, along the edge, and may also be made on the surface of a body. It may be found that when we put a certain mark on the edge in contact with a certain mark on the body, the scale can be turned so that another mark on the body lies between two other consecutive marks on the edge. If now, no matter how the edge and the other body may be turned, this mark always lies between the same two marks on the scale, we may infer that this will be true in any subsequent trial. If the same is found to be true in subsequent trials with different marks, the body may

be called rigid, and the straight edge also may be said to be "on a rigid body."

An important method of testing "rigidity" is by means of such instruments as calipers or compasses. These being set with one point at a mark on the body, the other point may be made to mark out a curve on it. If in subsequent trials it is always found that when one point of the compasses is at one mark the other, if in contact with the body at all, touches it at some point on the curve already drawn, the body may be called "rigid." The compasses or calipers themselves, between adjustments, may be shown to be rigid bodies by comparison with a straight edge. Their use is indispensable in testing the rigidity of convex solids. Cases where the rigid body tests are not satisfied are not included in the subject matter of mensuration, but are dealt with in higher branches of mechanics.

We next require a rule for ordering distances. If we have two pairs of marks, A and B on one body, C and D on another, and apply the caliper test to them, we may find that if the calipers are set so that one point can rest on A and the other on B at the same time, and if one point is then applied to C and a curve marked out on the body with the other point, D is either within, on, or outside this curve. If it is within it, we agree to say that the distance AB is greater than CD; if it is on it, that they are equal; and if it is outside it, that AB is less than CD. The process may be inverted. We can establish experimentally in this way that  $AB=BA$ ; that if AB is greater than CD, then CD is less than AB; and that the relations greater than, equal to, and less than, are transitive. Thus these three propositions, which are postulates in most metrical geometries, are experimental facts in mensuration. We have then arrived at a definition of what is meant by saying of two distances that one is greater, less than, or equal to the other.

In the above account the straight edge has been treated as anterior to the rigid body, whereas it might appear that the opposite procedure would have been the more natural. The arrangement which has been adopted here appears to be necessary, on account of a difficulty in the comparison of distances. In order to establish directly that the distance associated with one pair of marks  $ab$  is less than the distance associated with another  $cd$ , it is necessary to place the bodies bearing them in such a position that one can observe that neither  $a$  or  $b$  is outside  $cd$ . This can be done only if at least one of the pairs  $ab$ ,  $cd$  is connected by a straight

edge; for otherwise the marks may only be missing each other as the bodies are turned about, without  $a$  or  $b$  ever being between  $c$  and  $d$  at all.

*The Numbering of Distances.*

The facts of experience and the principle of empirical generalization therefore enable us to build up a theory of mensuration from the primitive idea and a few simple postulates. We may now go on to consider the way in which more complicated results may be obtained. We have so far considered only the relations greater than, less than, and equal to between distances on rigid bodies associated with marks. We now propose to build up a quantitative system of measurement such as is used in scientific instruments.

If we take any two straight edges, we can make marks along them when in contact so that to every mark on each there corresponds one on the other in contact with it. The results already enunciated are enough to establish the proposition that if the distance between two points on a rigid body is between the distances from the first mark on one of these edges to the  $n$ th and the  $(n+1)$ th respectively, it will also lie between the distances on the other scale that corresponded to these in the test. Further, it is not necessary that scales should have been directly compared. It is sufficient that they should have been compared to the same scale. Hence, if we have one standard scale, it is possible to make others to its pattern, and by means of them to assign an order to all distances sufficiently small to come within the scope of any of them. Similarly, the caliper method may be used to compare distances on a body with those on a scale, the calipers when set to one adjustment being a rigid body within the definition.

So far the scales considered have been graduated arbitrarily, and the results apply equally to all methods of graduation. There is one special type that offers great advantages over all others. If two distances  $a$  and  $b$  are set off along a straight edge from the point  $o$ , a definite mark is reached; this is experimentally verifiable. If the same two distances are set out in the reverse order,  $b$  first and then  $a$ , it is found that the same mark is reached. This is a new result, and is not a consequence of our previous ones. Repeated experimental confirmation, however, enables us to attach practical certainty to inferences from it. It is also found that however many distances are set out along a

straight edge in this way, the order in which they are set out makes no difference to the point where we finish. These facts suggest a relationship to the numerical process of addition. We can make marks along a straight edge so that every distance from a mark to the next is the same, except of course in the case of the last one, where there is no such distance. Such a marked edge may be called a uniformly graduated scale. The measured distance from one point to another can now be defined as the number of such intervals along this edge that it can be made to overlap, when compared with the edge by rigid body displacements. The measured length of a segment of a straight edge may also be defined as the measured distance between its ends. In consequence of the results of this paragraph, the measured length of any segment of a straight edge is equal to the sum of the lengths of any segments into which it may be subdivided (with slight errors, small in comparison with the whole length when the measured length is great). Thus numerical addition is applicable to measured lengths.

The measuring scales used in laboratories are just such scales as we have been describing. In the process of manufacture the successive divisions are marked off automatically, so that the marks can be made to touch simultaneously consecutive turns of a screw, which is a rigid body according to the definition adopted in this paper. Further, this can be done whatever mark we start with, so that the screw serves also as our intermediate body for the comparison of one segment of the straight edge with another, and the length of every segment is thus found to be the same. The process of manufacture of the screw is itself such that every turn is compared with a standard body, to which all the intervals on the scale are therefore ultimately referable. Thus laboratory scales are uniformly graduated scales, and measures made with them come within the subject matter already marked out.

A definition of relative motion is not required at this stage. We are dealing only with cases where the measured distances are found, on repetition of the process of measurement, not to vary. Hence the absence of relative motion among the parts of a system has already been included in the specification of the problem.

It may be objected that there are many bodies which do not satisfy the conditions we have specified. It is, however, an experimental fact that there are many bodies which do satisfy them. These bodies form the subject matter of the



theory of mensuration. Other bodies which do not satisfy these conditions obviously exist, but their treatment is a matter for other branches of physics.

In many cases it may turn out that a distance whose value has been inferred according to the rules which have been enunciated above cannot actually be measured, on account of the impossibility of carrying out some physical construction. This affords no objection to the methods in question. If it is possible to carry out the construction, the methods here elaborated predict what the measure will be. The physical construction required—if indeed any is required—may be regarded as part of the perceiving arrangement, and experiments which cannot be carried out as on a similar footing to sensations which cannot be perceived; they are not part of the subject matter of science.

*Can Mensuration be included in any known Geometry?*

While the development of mensuration differs from that of any existing geometry in its use of a principle of generalization, it may yet happen that when its elementary results have been generalized by this principle the generalizations may be found to agree with those of some known geometry. If this were so, the whole of it would constitute a class of entities and relations to which the body of propositions that constitute this geometry would be applicable. The only reservation to be made would be the one\* about inferred values lying within certain limits and not necessarily being exact. When we examine geometries, however, we find that there is none that satisfies our conditions. Consequently the whole of the theory of mensuration must be developed from the beginning.

All projective and descriptive geometries are evidently ruled out at once. A requirement of all such geometries is that no notion analogous to distance is to be used. Since distance forms our subject matter, there is no common ground whatever.

Euclid's geometry is the closest existing analogue of mensuration, and a more detailed discussion of it is desirable. The notion of length is freely used in it, being treated as undefined. His points are sufficiently like our marks, and his straight lines are sufficiently like our straight edges. His unstated axiom of superposition is practically what we have adopted as an experimental fact for rigid bodies.

Nevertheless Euclid's geometry is not applicable to

\* Phil. Mag. vol. xlv. pp. 368-374 (1923).

mensuration. His "length" is applied to curves as well as to straight lines (see Prop. VI. 33), which we have not yet had occasion to do; but in fact most of his applications are to straight lines. He postulates that every straight line has a length. The corresponding proposition in mensuration is true; for though we can deal only with measures of length, and it happens sometimes that a straight edge is longer than any available measuring scale, we can always repeat the application and by an analogue of the well-known postulate of Archimedes continue until the whole of the edge has been overlapped, and a measure is then obtainable. But he postulates further that any two points can be joined by a straight line. The analogue of this is often true, but in the case of a convex body too hard to be bored it is not possible to construct a straight edge that extends from one to the other. Yet the distance between these marks exists, for it can be measured by the caliper method. Thus Euclid's treatment fails to satisfy the condition stated in a previous paper\* to be essential to any scientific theory—namely that of being applicable in practice to the subject matter with which it is proposed to deal.

The most important departure of Euclid's treatment from any possible account of mensuration, however, is in the discussion of parallels and the related propositions. We refer especially to the fifth postulate, also called the twelfth axiom, and to the second postulate, that a straight line may be produced to any length, however great. Both of these postulates have been criticized by modern geometers as not obvious. In mensuration, on the other hand, they are not only not obvious but demonstrably false. The length to which we can produce a straight edge is limited by the size of the body of which it forms part; it may be extended by fastening other bodies on, but there is a limit to this process, and therefore to the length of a straight edge. Again, it may be possible to find out by our existing methods of measuring angles that, when one straight edge crosses two others, it makes the sum of the interior angles less than two right angles, but it does not happen in all such cases that the two straight edges it crosses intersect; for in fact they are often too short, or they may not be in one plane—a detail that is not allowed for in the usual statements of the postulate.

The alternative known as Playfair's axiom does not meet

\* Phil. Mag. vol. xlii. pp. 369-390 (1921).

the difficulty, for it is not true that of two intersecting straight edges at least one must intersect any other; Playfair's parallel axiom fails in just the same way as Euclid's.

An alternative method would be to adopt as an experimental fact, which it may seem to many to be, that the sum of the angles of a triangle is equal to two right angles. We do not wish to deny that an account of mensuration may be constructed on these lines; but we do not think it is the best way of constructing one. So far we have not had occasion to specify how angles are to be measured. Euclid gives no method of measuring them, but assumes in the course of his proofs several propositions about them that amount to such a method. He supposes in I.4 that angles that can be superposed are equal; and in I.13 that if a pencil of coplanar lines is drawn through a point, the angle between the extreme lines is equal to the sum of those between consecutive lines of the pencil. In other words, he supposes that there is a quantity associated with any pair of lines which is the same for superposable pairs on rigid bodies, and is additive for sheaves of angles in a plane. This can be proved experimentally in many cases by means of the protractor.

This method is, however, of very limited application in practice. The angles can only be superposed in special cases; projections on the rigid bodies that carry them usually interfere with it. Again, the truth of the addition proposition rests on the angles to be added being placed in the same plane; thus the measurement of angles is posterior in knowledge to the notion of a plane, and we require a rule that will enable us to recognize a plane when we meet one. Euclid's definition is that a surface is plane if any straight line joining two points of it lies wholly upon it. But, in the case we are thinking of, projections will again nearly always interfere with the application of this test. Hence the notion of a plane, and with it that of the direct measurement of angles, should be avoided in a development of mensuration if it can be managed.

In a paper recently published\* a very different view of Euclid is taken. It is however admitted (p. 28) that several of Euclid's postulates are experimentally false.

\* Campbell, *Phil. Mag.* vol. xliv. pp. 15-29 (1923).

*The Development of a Theory of Mensuration.*

In our discussion of mensuration we have, so far, arrived only at methods of comparing distances, estimating them quantitatively by comparison with uniformly graduated scales, and at propositions about distances along the same straight edge. The way in which real numbers may be applied to the distances associated with pairs of points may be exhibited in the following postulates and definitions:—

1. To each pair having a distance, one and only one number belongs.
2. If the number  $n$  belongs to the pair  $(x, y)$ , then it belongs also to the pair  $(y, x)$ .
3. If the distance between one pair of points is not greater than that between another pair, then the number belonging to the first is not greater than the number belonging to the second.
4. If two pairs  $(x, y)$ ,  $(y, z)$  are such that  $xyz$  are in the same straight line (with  $y$  between  $x$  and  $z$ ), then the number belonging to the pair  $(x, z)$  is the sum of the numbers belonging to the distances associated with the pairs  $(x, y)$ ,  $(y, z)$ .
5. The number 0 is to belong to the distances associated with pairs in which the two constituents are identical.
6. The number 1 is to belong to the distance associated with a certain pair called the unit pair.

Thus any one system in the theory we are suggesting would involve these postulates, together with some arbitrary choice of the unit pair defined in 6. Thus the Metric system and the British system differ only in the fact that in the arbitrary choice of the unit pairs the unit pair selected in the one system was not congruent to the unit pair selected in the other system. Thus, if the actual marks corresponding to these unit distances were placed side by side, the marks would not be superposable.

With these postulates and definitions, we write for the number belonging to the pair  $(x, y)$  the symbol  $xy$ . Thus we have

$$xy = yx,$$

$$xx = 0.$$

It is worth while to point out that the assertion

$$xy = 1$$

means that the pair  $(x, y)$  is the actual pair chosen as the

pair to have unit distance associated with it or congruent to it.

When the postulates governing the number of distances have been specified, it is permissible to use all algebraic and arithmetical operations. It will therefore not be necessary to define, for example, what is meant by the square of a number\*. Arithmetic and Algebra are taken over in their entirety.

The account which was given on p. 9 of the development of the idea of distance arose directly out of notions which can evidently be reduced to the one primitive notion of "not greater than." In introducing measurement, we have had to introduce a further notion, namely that of a fixed standard of reference. This standard could have been chosen in many ways from the pairs available, and it is not as a rule specified by previous experience. If a different standard is chosen, different numbers are found. Thus our measures are apparently influenced by convention. It can readily be inferred from the results already stated, or it may be directly verified, that a change of standard alters all the numbers in measures in the same ratio. Accordingly, the conventional choice of a unit of distance does not influence the ratios of the numbers involved in measures of distance, and therefore if we discover any physical law homogeneous in these numbers that is true with one unit, it will be true whatever other unit is chosen. We shall, in fact, use only such laws in the development of the subject. It could not have been predicted beforehand that any law would exist that would involve only homogeneous functions, so that the unimportance of convention is in this case, as in all others, a matter of experimental verification rather than of *a priori* necessity. On the other hand, in inferences from laws it will be necessary to obtain the actual measure in terms of some particular unit; in this case the unit must of course always be specified, for otherwise the result would be meaningless.

We also require propositions about the relations between the distances from each other of marks not in the same straight edge. This introduces a new domain, and we need at least one new experimental fact to serve as a starting point. As has already been indicated, propositions involving angles or planes should be avoided if possible. We therefore need an experimental fact dealing

\* This and other relevant definitions are given in 'Principia Mathematica,' Whitehead and Russell, Cambridge. Cp. \*91, where the square of a relation is defined.

with distances. The most suitable appears to be the following:—

Let two straight edges meet in  $o$ . Let  $x$  be a mark on one edge, and  $y$  a mark on the other. Then, whatever  $ox$  and  $oy$  may be,

$$\frac{\partial}{\partial ox} \left( \frac{ox^2 + oy^2 - xy^2}{2ox \cdot oy} \right) = 0,$$

$$\frac{\partial}{\partial oy} \left( \frac{ox^2 + oy^2 - xy^2}{2ox \cdot oy} \right) = 0,$$

and each ratio is not greater in absolute value than 1.

This proposition lacks the chief qualification of a primitive proposition in a geometry—namely, that of possessing a *naïveté* that disarms suspicion. For our purpose, on the other hand, it has the great advantages that it is capable of experimental test in almost all cases, and that such test has already been carried out in countless experiments in practical plane “geometry.” So far as we know, it has not been tested with the full accuracy of which modern measuring apparatus is capable, but enough has been done to establish it in an enormous number of cases. It is not extremely simple in form, but the number of verifications is so great that if its prior probability is at all appreciable, the probability of all inferences from it must amount to practical certainty. We therefore suppose it to hold in general, and attempt to develop its consequences.

Instead of working with the ratio itself, it is often convenient to use a certain known function of it. If the straight edges  $oa$ ,  $ob$  meet in  $o$ , we put

$$\frac{oa^2 + ob^2 - ab^2}{2oa \cdot ob} = x.$$

We can now define the measure of the angle  $aob$  to mean  $\int_x^1 \frac{du}{(1-u^2)^{\frac{1}{2}}}$ . This is a known function denoted in pure mathematics by  $\cos^{-1} x$ . The path of integration is confined to real values of  $u$ , and the positive sign is taken for the root, so that no difficulty of interpretation arises. Then we have

$$\cos aob = x,$$

$$\sin aob = + (1-x^2)^{\frac{1}{2}}.$$

It is evident from our premises that the measure of an angle is the same whatever marks on its arms we use in our length-measurements.

1. If two straight edges meet, the adjacent angles are together equal to  $\pi$ .

Let  $a$  be a mark on one edge, and  $b_1$  and  $b_2$  marks on the other, such that  $o$  the junction of the edges lies between them. We have

$$ab_1^2 = oa^2 + ob_1^2 - 2oa \cdot ob_1 \cos aob_1, \quad \dots \quad (1)$$

$$ab_2^2 = oa^2 + ob_2^2 - 2oa \cdot ob_2 \cos aob_2, \quad \dots \quad (2)$$

$$\text{and also} \quad = ab_1^2 + b_1b_2^2 - 2ab_1 \cdot b_1b_2 \cos ab_1b_2. \quad \dots \quad (3)$$

$$\text{Now} \quad b_1b_2 = b_1o + ob_2, \quad \dots \quad (4)$$

$$\begin{aligned} \cos ab_1b_2 &= (ab_1^2 + ob_1^2 - ao^2) / 2ab_1 \cdot ob_1 \\ &= (ob_1 - oa \cos aob_1) / ab_1 \quad \dots \quad (5) \end{aligned}$$

by (1).

Substituting in (3) from (1), (4), and (5), we have

$$ab_2^2 = oa^2 + ob_2^2 + 2oa \cdot ob_2 \cos aob_1. \quad \dots \quad (6)$$

Thus by comparison with (2) we find

$$\cos aob_2 = -\cos aob_1;$$

whence

$$aob_1 + aob_2 = \pi. \quad \dots \quad (7)$$

2. It follows as an immediate corollary by Euclid's method that when two straight edges cross, the opposite angles are equal.

3. The sum of the angles of a triangle is equal to  $\pi$ .

Consider any triangle  $abc$ . Put  $bc + ca + ac = 2s$ .

Then, defining the tangent as the ratio of sine to cosine and transforming as in trigonometry, we find

$$\tan \frac{1}{2}bae = \left\{ \frac{(s-ab)(s-ac)}{s(s-bc)} \right\}^{\frac{1}{2}},$$

with two symmetrical relations. Hence, by the properties of the tangent, we can find

$$\begin{aligned} \tan \frac{1}{2}(bac + bca) &= \left\{ \frac{(s-ca)}{(s-ab)(s-bc)} \right\}^{\frac{1}{2}} \\ &= \tan \frac{1}{2}(\pi - abc). \end{aligned}$$

Whence

$$bac + abc + bca = \pi.$$

4. If two straight edges  $oa$  and  $ob$  meet at  $o$ , and if  $\cos aob$  is negative, and if  $o$  is not the end of  $ob$ , it is possible to make a mark  $b_1$  on  $ob$  such that  $\cos aob_1$  is positive.

For by Prop. 1 we need only take  $b_1$  on the side of  $o$  opposite to  $b$ , when the result follows.

5. If  $a$  be outside the edge  $ob$ , and if  $b$  be on that part

of it for which  $aob$  is less than  $\frac{1}{2}\pi$ , and if  $ob$  be greater than  $oa \cos aob$ , then it is possible to make a mark  $c$  on  $ob$  such that  $oa^2 = oc^2 + ac^2$ .

For we can make a mark  $c$  on  $ob$  at a distance  $oa \cos aob$  from  $o$ . Then

$$\begin{aligned} ac^2 &= oa^2 + oc^2 - 2oa \cdot oc \cos aob \\ &= oa^2 - oc^2, \end{aligned}$$

which proves the proposition.  $\square$

We can now introduce the definition of perpendicularity. If the angle between two straight edges is  $\frac{1}{2}\pi$ , they are said to be perpendicular. Df.

If  $oa$  is a straight edge, with a mark  $c$  on it so that the angle  $bco$  is  $\frac{1}{2}\pi$ , where  $b$  is some mark not on the edge, the mark  $c$  is called the foot of the perpendicular from  $b$  to the edge. Df.

6. If two straight edges  $oa, ob$  intersect at  $o$ , and  $c$  is any mark in one of them; if also the length of the other exceeds  $oc \sec \angle aob$ , then we can make a mark  $d$  on it so that  $c$  is the foot of the perpendicular from  $d$  to the first line.

For we can make a mark  $d$  such that  $od = oc \sec aob$ , and the perpendicularity follows by the method of Prop. 5.

7. If the angle  $aob$  is  $\frac{1}{2}\pi$ , we have at once

$$\begin{aligned} ob &= ab \cos abo, \\ oa &= ab \sin abo, \\ oa &= ob \tan abo, \end{aligned}$$

with corresponding formulæ for the other trigonometric functions. These results thus emerge as laws, and not as definitions as in ordinary discussions.

8. Consider three edges meeting together in  $o$ . It is always possible to fix  $a$  in one of them so that  $a$  is the foot of the perpendiculars from points  $b$  and  $c$  on the other two, since the condition of Prop. 6 can always be fulfilled by making  $oa$  short enough.

Then

[illegible]

[illegible]

$$ac = oa \tan aoc, \quad (3)$$

[illegible]

$$\begin{aligned} bc^2 &= ob^2 + oc^2 - 2oa \cdot oc \cos boc \\ &= oa^2 (\sec^2 aob + \sec^2 aoc - 2 \sec aob \sec aoc \cos boc). \quad (5) \end{aligned}$$



Also

$$\begin{aligned} bc^2 &= ab^2 + ac^2 - 2ab \cdot ac \cos bac \\ &= oa^2(\tan^2 aob + \tan^2 aoc - 2 \tan aob \tan aoc \cos bac). \quad (6) \end{aligned}$$

Equating these two expressions, and multiplying by  $\cos aob \cos aoc$ , we find that

$$\cos boc = \cos aob \cos aoc + \sin aob \sin aoc \cos bac.$$

This is the analogue in mensuration of the well-known formula of spherical trigonometry.

It follows as a corollary that  $bac$  is independent of  $oa$ .

9. If  $bac$  forms a straight edge,  $\cos bac$  is  $-1$ , and we have

$$\begin{aligned} \cos boc &= \cos aob \cos aoc - \sin aob \sin aoc \\ &= \cos (aob + aoc); \end{aligned}$$

whence the measure of  $boc$  is the sum of those of  $boa$  and  $boc$  if their sum does not exceed  $\pi$ ; if it exceeds  $\pi$ ,

$$boc + aob + aoc = 2\pi.$$

We have thus proved that angles can be added if the same straight edge intersects their arms; this proposition, which is fundamental in Euclid's treatment, emerges here as a special case of Prop. 8.

If three straight edges have a mark in common and a fourth straight edge not through this mark intersects all three, they are said to lie in one plane. Df.

Any mark that a straight edge can pass through and intersect two other straight edges is said to be in the same plane as these straight edges. Df.

The angle between two edges both perpendicular to the same edge is called the angle between the planes containing this edge and the first two. Df.

It will be noticed that we have not defined the term "plane" as such, but only the expressions "lie in one plane," "in the same plane," and "angle between the planes." Thus we can attach meanings to these terms even though no physical plane has been constructed.

10. Consider any two points  $l$  and  $m$ , and a straight edge  $op$ . Suppose points  $a$  on  $op$ ,  $b$  on  $ol$ ,  $c$  on  $om$  to have been found, such that  $ba, ca$  are perpendicular to  $op$ . Let  $ol = r, om = r', \angle lop = \theta, \angle mop = \theta'$ . Then

$$\begin{aligned} lm^2 &= r^2 + r'^2 - 2rr' \cos lom \\ &= r^2 + r'^2 - 2rr'(\cos \theta \cos \theta' + \sin \theta \sin \theta' \cos bac). \quad (1) \end{aligned}$$

If  $ak$  be any other straight edge through  $a$ , such that  $kabc$  are in a plane, let angle  $kab = \phi$ ,  $kac = \phi'$ . Then

$$bac = \phi - \phi'.$$

Hence

$$\begin{aligned} lm^2 &= r^2 + r'^2 - 2rr'\{\cos \theta \cos \theta' + \sin \theta \sin \theta' \cos (\phi - \phi')\} \\ &= (r \cos \theta - r' \cos \theta')^2 + (r \sin \theta \cos \phi - r' \sin \theta' \cos \phi')^2 \\ &\quad + (r \sin \theta \sin \phi - r' \sin \theta' \sin \phi')^2. \quad \dots (2) \end{aligned}$$

We can regard  $oa$  as our initial line, and  $oa$  and  $ak$  as lying in our initial plane. Then (1) is the standard formula for the distance between two points in spherical polar co-ordinates.

We can also define  $xyz$  as follows :—

$$x = r \sin \theta \cos \phi, \quad \dots \dots \dots (3)$$

$$y = r \sin \theta \sin \phi, \quad \dots \dots \dots (4)$$

$$z = r \cos \theta. \quad \dots \dots \dots (5)$$

Then

$$lm^2 = (x - x')^2 + (y - y')^2 + (z - z')^2. \quad \dots (6)$$

The distance has thus been expressed in the standard form appropriate to Cartesian coordinates.

The above definition of Cartesian coordinates is applicable in all cases where it is possible to find the distances and bearings of our points, whereas the usual definition is not applicable except where we can actually find the perpendiculars from the points to the three coordinate planes. We still have to show that  $x$ ,  $y$ , and  $z$  are actually Cartesian coordinates according to the usual definition on those occasions when this can be applied.

11. If a straight edge be perpendicular to two straight edges that meet it, it is perpendicular to any other straight edge that meets it in the plane of these two. The proof of *Euc. XI. 4* is readily adapted to prove this. In such a case the first edge may be said to be perpendicular to the plane.

12. Consider any marks  $p$ ,  $q$  with spherical coordinates  $(r_1, \theta_1, \phi_1)$   $(r_2, \theta_2, \phi_2)$ . The condition that  $op$ ,  $oq$  shall be at right angles is that

$$pq^2 = op'^2 + oq^2.$$

Thus

$$2r_1r_2\{\cos \theta_1 \cos \theta_2 + \sin \theta_1 \sin \theta_2 \cos (\phi_1 - \phi_2)\} = 0,$$

or

$$x_1x_2 + y_1y_2 + z_1z_2 = 0.$$

13. At any point on the initial line,  $y$  and  $z$  are clearly zero. Hence at any point in the plane through  $o$  perpendicular to this line we must have  $z=0$ .

Let  $p$  be any point  $(x_1, y_1, z_1)$  and  $q$  any point  $(x_2, y_2, 0)$  in this plane. Then

$$pq^2 = (x_1 - x_2)^2 + (y_1 - y_2)^2 + z_1^2.$$

Evidently this is least for a given position of  $p$  if

$$x_2 = x_1 \quad \text{and} \quad y_2 = y_1.$$

Then we see that the shortest distance of  $p$  from the plane  $z=0$  is  $z$ . Similarly we can show that when  $\phi=0$  we have a plane such that  $y$  is 0 for all points on it, and that the shortest distance of  $p$  from this is  $y_1$ ; and similarly for  $z$ . Thus the Cartesian coordinates are the shortest distances of the point considered from three fixed perpendicular planes.

Since the shortest distance of  $p$  from any point on the plane must be at least as short as the shortest distance from the point to any line in the plane, it follows that the shortest straight edge that can extend from  $p$  to a plane must also be the shortest distance of  $p$  from every straight edge in the plane that meets it, and therefore, by Prop. 5 and the definition of perpendicularity, must be perpendicular to every such straight edge, or, by the definition under Prop. 11, to the plane.

Thus the Cartesian coordinates have been identified with those defined in the usual way.

## II. *The Absorption produced by Electrically Luminescent Sodium Vapour.* By F. H. NEWMAN, D.Sc., A.R.C.S., Professor of Physics, University College, Exeter\*.

[Plate I.]

### 1. *Introduction.*

ALTHOUGH the Bohr theory of the atom has not yet been developed to give a complete representation of the spectra of elements other than those of hydrogen and helium, it gives a general indication of their structure. The difficulties involved in their calculation have not been overcome at present. The 1.5 S ring of an atom represents the stable orbit, and all the lines contained in the series 1.5 S —  $mp$  are emitted when the electrons in different atoms fall from one of the  $p$  rings to the 1.5 S ring. The first subordinate

\* Communicated by the Author.

series lines are produced by electrons falling from the  $md$  rings to the  $2p$  ring, and the second subordinate series when the electrons fall from the  $ms$  rings to the  $2p$  ring. Inter-orbital motions other than those mentioned give rise to combination lines and the fundamental series. The  $1.5 S$  ring represents the outermost stable orbit in the normal atom, and the innermost unstable orbit. In order that the electron shall be ejected from the  $1.5 S$  ring to the next orbit—the  $2p$  ring,—the atom must receive energy either by bombardment, or by the absorption of radiation, equal to 2.09 volts in the case of sodium. The electron within the atom being now in an unstable orbit falls to the  $1.5 S$  ring, and in so doing gives up the quantum of energy received during its ejection from the  $1.5 S$  ring, as a quantum of radiation  $h\nu$ , with the emission of the D lines. When energy equal to or greater than 5.12 volts is communicated to the atom, the valency electron in the atom is displaced from the  $1.5 S$  ring to infinity, and in returning may occupy any one of the multitude of stationary states, the dimensions of which are large compared with the orbits of the other electrons, within the atom, before it finally reaches the stable orbit. The many electrons returning in the different atoms will do so by various paths, and we obtain the many line spectra, the intensities of the lines representing to some approximation the chances of the inter-orbital transitions. As at present only two potentials, viz. the resonance potential and the ionizing potential, have been observed for sodium vapour, it seems probable that there are only two ways in which the electron may move within the atom when being ejected from the  $1.5 S$  ring. It is ejected to the first  $p$  ring, or it is removed to infinity. This applies when electrical stimulus is employed.

The lines of the principal series of sodium are all absorption lines, and no line of any other series has been reversed, although recently Datta \* has shown that the two combination lines  $1.5 S-2d$  and  $1.5 S-3d$  of potassium are absorbed when light from an electric arc is passed through potassium vapour. The excitation of these lines is well known, and previously it was thought that they appeared owing to the presence of the electrostatic field, as they represent inter-orbital transfers requiring two units change in azimuthal quantum, which is inadmissible according to the selection principle of Bohr. Foote, Meggers, and Mohler † have shown also that the combination line  $1.5 S-2d$  may be

\* Proc. Roy. Soc. A. vol. ci. (1922).

† Phil. Mag. vol. xliii. (1922).

produced in a low voltage arc where the external electric field cannot be effective. It has been pointed out by Bohr \*, however, that this line was only excited in the experiments when the electron density was very great. In this case the fields due to the neighbouring positive ions and electrons, to which the emitting atoms are subject, may have been many times greater than the intensity of the external electric force present due directly to the applied potential difference.

The radiation quanta absorbed are able to remove the electron to any of the  $p$  orbits within the atom, and so the energy absorbed may be very nearly that required to ionize the atom. On the return of the electron to its stable orbit radiation energy is emitted, and is observed as fluorescence. In this way Rayleigh † has excited the fluorescence of sodium vapour by the 5896, 5890 lines, and also by the 3303 line. It thus appears possible to do by absorption what cannot be performed by electron impacts, namely, displace the electron to any of the  $p$  orbits.

Low voltage arcs in metallic vapours suggest that it is possible to eject the electron to infinity from the  $2p$  ring, for these arcs operate at a potential below the ionizing potential. The energy necessary to eject the electron from this orbit will certainly be less than that required if the electron is in the  $1.5$  orbit. The energy necessary for the transfer to the  $2p$  ring may be obtained from the bombardment by an electron having energy equal to the resonance potential, or by the absorption of radiation  $h\nu$  from adjacent atoms which are in the partially ionized condition. Atoms of metallic vapours seem to permit of the radiant energy liberated by each electron impact which results in radiation, to be passed on from atom to atom, and this multiplies the fraction of atoms which are in the abnormal or partially ionized condition. The greater part of the radiation emitted when electrons fall from the  $2p$  to the  $1.5$  S rings will escape from the tube, but some of it may be taken up by neighbouring atoms. This absorption effect will increase with the vapour-pressure, and with an increase in the density of the bombarding electrons. Under these conditions many of the valency electrons of the atoms will be in the  $2p$  rings, and so absorption of the principal lines will not occur, but rather those lines belonging to series converging to  $2p$  will become absorption lines. Theoretically then, if sodium vapour at a fairly high pressure is excited by a dense stream of electrons, and white light passed through the luminescent

\* Phil. Mag. vol. xliii. (1922).

† Strutt, Proc. Roy. Soc. A. vol. xcvi. (1919).

vapour, the subordinate series lines should show absorption. This was first suggested by Foote and Mohler\*.

Low voltage arcs always require a higher applied potential difference to start them than is necessary for their maintenance once they are started. After the initial discharge the ions present, together with the electrons, may produce internal electric fields far greater than the external applied electric force. On the theory of the radiation absorption, part of the energy for ionization is obtained from the radiation emitted by those atoms already ionized, so that less applied electric force is required after the initial discharge.

Pflüger†, using a condensed electric discharge in a three-electrode tube in which a short constriction provided the source of radiation and the wider and longer part the absorbing column, investigated the absorption and reversal of the hydrogen lines. He succeeded in reversing  $H\alpha$ . Kuch and Retschinsky‡, Pflüger§, and Grebe|| found that luminescent mercury vapour absorbed lines which were different from those absorbed by ordinary mercury vapour.

Robertson¶, using a sodium vapour electric discharge-tube described by the author, excited fluorescence in sodium vapour contained in another quartz tube. White light was passed through the latter, and the absorption spectra noted when the sodium vapour was fluorescing, and when it was not. There was no change in the absorption spectra, and no absorption of the subordinate series lines occurred. This was probably due to the small amount of fluorescence produced, with the result that comparatively few of the atoms had the valency electron ejected to the  $2p$  ring, and so few were in a condition to absorb radiation corresponding to those lines which converge to this limit.

## 2. Experiments.

It was thought that an experiment similar to that performed by Pflüger with hydrogen, but using sodium vapour instead of the gas, might show peculiar absorption effects. A quartz tube about 50 cm. long with a narrow constriction at one end was used, and a condensed electric discharge was sent through the sodium vapour maintained at  $300^{\circ}$  C. The light from the constriction was viewed through a quartz

\* *Phil. Mag.* vol. xl. (1920).

† *Ann. der Phys.* Bd. xxiv. (1907).

‡ *Ann. der Phys.* Bd. xxii. (1907).

§ *Ann. der Phys.* Bd. xxvi. (1908).

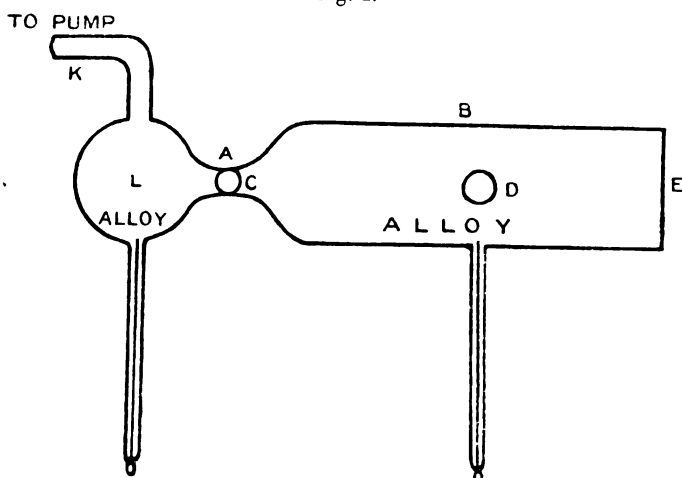
|| *Ann. der Phys.* Bd. xxxvi. (1911).

¶ 'Nature,' Jan. 1922, p. 43.

window at the end of the wider portion of the tube. The D lines alone showed self-reversal, and passing white light along the length of the tube simply gave absorption of the same lines. Here again the density of the free electrons within the tube is comparatively small. Another experiment using the principle described by the author \* in the sodium-potassium vapour arc-lamp was tried.

The apparatus is shown in fig. 1. It was made of quartz. The constriction A was 3 mm. in diameter, and the wider portion B 2.5 cm. in diameter and 20 cm. long. The

Fig. 1.



end of the wide portion was closed by a quartz window E fused to the end of the tube. Side tubes at C and D closed by quartz windows permitted the observation of the arc at different places. The alloy of sodium and potassium was introduced into the apparatus at K, and after evacuation of the apparatus, the alloy was run from L into B. Warming the alloy in L caused the oxide formed on the surface to disappear, and in this way the two pools of alloy had clean surfaces. With this arrangement an arc could be struck between the two alloy electrodes with an applied potential difference as low as 30 volts. The arc was struck by warming the alloy, connecting one electrode to a small induction coil, and passing a momentary electric discharge. Sometimes the arc could be started by simply tilting the apparatus, and so making momentary contact between the

\* Phil. Mag. vol. xlv. (1922).

two alloy electrodes. Once started the arc could be maintained for an indefinite period. The apparatus was placed inside an electric heater, so that the vapour pressure of the sodium within could be maintained at any desired value. Visual observations of the series produced were made at A, D, and E, and the spectrograms photographed with a constant deviation type of spectrometer, using Wratten panchromatic plates.

### 3. *Experimental Results.*

Under all experimental conditions the potassium lines were faint compared with those of sodium, but became relatively brighter as the applied potential difference was decreased. The radiations appearing at A had the characteristic colour of the D-line radiation, but observed at D the colour changed to a pale greenish-yellow. At A the D lines were very intense compared with all other lines, but at D the subordinate series lines of sodium and potassium appeared much brighter, although the concentration of the luminous sources must be much greater at A. This was most marked with high current densities, and is illustrated in the spectrograms shown in Pl. I. The relative intensity of the various lines when the radiation was observed through the window E was intermediate between that at A and D. As the current density decreased the relative brightness of the D lines increased. Raising the temperature of the apparatus to  $450^{\circ}$  C. caused strong self-reversal of the D lines as seen at E, but no self-reversal of any other lines. An electromagnet was arranged so that the luminous column in the constriction A was squeezed to that part of the tube away from the window C. This caused self-reversal of the D lines owing to the light passing through the intervening layer of cooler vapour before it emerged at the window C. Even with this arrangement, however, the D lines were still very bright compared with the other lines.

The radiation issuing at C had passed through a shorter length of absorbing vapour than that coming out at D and E, but the subordinate lines were very faint. It must be remembered, however, that the D light at E had suffered considerable absorption, since it had been transmitted through a considerable thickness of sodium vapour. It was to be expected, therefore, that the D lines would appear faint compared with the other lines.

The luminous sources in the constriction A are concentrated, and so the subordinate series lines should appear



intrinsically brighter at A than at D. Such is not the case. This can be explained if these lines are self-reversed, as seen at A. At the constriction the current density is high, and so the electrons are very dense. This is the condition for the absorption of the D-line radiation by atoms from neighbouring atoms. Many of the atoms present will thus be in the condition that the valency electron has been displaced to the  $2p$  ring, and so these atoms are no longer in a condition to absorb the D-line radiation, but rather those lines converging to  $2p$ . Thus the light transmitted by these atoms suffers absorption of the subordinate lines, while the D lines are not affected. In the wider portion of the apparatus the electrons are less dense. There is less chance of the atoms absorbing radiation, and so the subordinate lines no longer show self-reversal. Accordingly, they will appear brighter than at the constriction.

When the current in the arc is reduced, the density of the electrons and the self-reversal of the subordinate lines are less marked. This is illustrated in the spectrograms IV., V. (Pl. I.).

While the arc is in operation the actual drop of potential across the electrodes is only about 10 volts. At  $300^{\circ}$  C. the vapour pressure of sodium and potassium is high, and the mean free path of the electrons must be very small. It seems improbable that the bombarding electrons can gain energy sufficient to ionize during the time that this path is traversed. It is more likely that the atoms become partially ionized by the absorption of radiation. The atoms which are in this condition, *i. e.* those in which the valency electron is in the  $2p$  ring, will then require less energy than 5.1 volts for complete ionization.

White light from an arc was passed through the radiation at the constriction, and also at D, and the complete spectrum viewed at the windows C and D. Visual observations showed absorption of the D lines only, they of course appearing dark on the luminous background.

The light issuing at D came from a point within the tube at a considerable height above the alloy electrode. There was no possibility of the variation in the relative intensity of the lines being due to the electrode potential gradient.

The spectrograms I., II., III. (Pl. I.) were photographed with exposures of 10 seconds each, and those of IV., V. (Pl. I.) with 20 seconds' exposure.

III. *Diffraction Pattern in a case of two very close Point-Light Sources.* By B. E. MOURASHKINSKY, *Optical Laboratory of the Central Chamber of Weights and Measures, Petrograd* \*.

[Plate II.]

AS is well known, the illumination at the point  $r$  in the focal plane of a geometrically corrected object-glass with a circular aperture due to a point-light source is expressed by

$$I = M \frac{4J_1^2(z)}{z^2}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where

$$M = \frac{\pi^2 R^4}{\lambda^2 f^2}; \quad z = \frac{2\pi R}{\lambda f} r, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$R$  being the radius of the object-glass,  $f$  its focal length,  $\lambda$  the wave-length of light,  $r$  the distance of the considered point from the geometrical image of the point-source (in the focal plane),  $J_1$  Bessel's function of order unity. The illumination at the geometrical image of the source is assumed to be equal to unity.

For values of

$$\frac{4J_1^2(z)}{z^2} \quad . \quad . \quad . \quad . \quad . \quad (1a)$$

we have Lommel's tables, in which the argument is varying by tenths from  $z=0$  to  $z=20.0$ .

If we take two point-sources, primarily of equal intensity, and denote the illumination at the point  $r$  due to the first source by  $I_1$  and that due to the second by  $I_2$ , the entire illumination at this point due to both the sources will be

$$I = I_1 + I_2,$$

$$I = M \left[ \frac{4J_1^2(z_1)}{z_1^2} + \frac{4J_1^2(z)}{z^2} \right], \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$z = \frac{2\pi R}{\lambda f} r,$$

$$z_1 = \frac{2\pi R}{\lambda f} r_1,$$

where  $r$  and  $r_1$  are the distances of this point in the focal plane from the geometrical images of two sources.

\* Communicated by the Author, having been read before the Russian Astronomical Society, April 27, 1922.

The distribution of illumination along a meridional line (a line joining two geometrical images) depends on the distance between the sources. If the distance between two geometrical images is  $D$ ,

$$D = \frac{2\pi R}{\lambda f} d, \quad . . . . . (4)$$

$d$  being a linear distance between these images in focal plane; then

$$r_1 = d - r,$$

$$z_1 = D - z.$$

The value  $z$  may be either positive (towards the image of the second point) or negative (in the opposite direction). The expression (3) may be written

$$I = M \left[ \frac{4J_1^2(z)}{z^2} + \frac{4J_1^2(D-z)}{(D-z)^2} \right]. \quad . . . . . (5)$$

The factor  $M$  is constant for a given instrument, and the illumination at the point  $r$  will be

$$\frac{4J_1^2(z)}{z^2} + \frac{4J_1^2(D-z)}{(D-z)^2}. \quad . . . . . (6)$$

The measured angular distance between two point-sources expressed in arc seconds may be converted into  $D$  and *vice versa* by means of the following simple relations:

$$D = \frac{2\pi R}{\lambda} \frac{d}{f},$$

$$D = \frac{2\pi R}{\lambda} \frac{D''}{\tan 1''}, \quad . . . . . (7)$$

$$D'' = D \cdot \frac{\lambda}{2\pi R} \tan 1'' \quad . . . . . (8)$$

As two points are of equal intensity, the distribution of illumination along a meridional line will be symmetrical with respect to two geometrical images.

The question is, what value should  $D$  attain so that the two images would be just resolved.

The resolving power of an object-glass with a circular aperture depends on: (1) the size of an aperture, *i.e.* its diameter, (2) the wave-length of light of a source, (3) the contrast between the illumination at the geometrical images of two sources and that at the central minimum in the

diffraction-pattern. An object-glass with the radius  $R$  for one angular distance between two point-sources  $D''$  gives the distance  $D = \frac{2\pi R}{\lambda} \frac{D''}{\tan 1''}$ ; the other object-glass for the same angular distance gives another value of  $D$ . For each  $D$  we have the corresponding ratio of illumination (in the diffraction pattern) at its maximum to that at the central minimum. The eye can detect only a limit difference of illumination depending on its contrast sensibility.

The general theories of the resolving power state that two point-light sources of equal intensity are resolved when the maximum of illumination in the diffraction pattern due to one of them coincides with the first minimum in the diffraction pattern due to the other, *i. e.* when the distance between two geometrical images of such sources is equal to the radius of the first dark ring. Lord Rayleigh, in his paper "Wave Theory," admits as a limit of resolution a coincidence of the maximum of illumination in the diffraction pattern due to one object with the first minimum due to the other in all the cases of point and line sources for circular and rectangular apertures. In the case of two points we have the usual relations :

$$D = \frac{2\pi R}{\lambda} \frac{d}{f} = 3.8316,$$

$$\tan D'' = \frac{d}{f} = \frac{3.8316}{\pi} \frac{\lambda}{2R},$$

$$\tan D'' = 1.22 \frac{\lambda}{2R}. \quad . \quad . \quad . \quad . \quad (9)$$

This general relation is entered without any further consideration into many optical text-books, even into the best ones.

The resolving power of an object-glass is generally considered as the least angular distance between two objects at which the latter are just resolved, easily resolved, etc. These last terms introduce a great uncertainty as to what exactly is meant by resolution. If we admit the resolution as a complete separation (contact) of the central bright spots in the diffraction pattern, we must know the diameter of the visible part of the central spots, because we do not observe a first dark ring as a geometrical circumference, but it has a sensible width. The diameter of the visible part of a central spot depends on the threshold sensibility of the eye for a case of the diffraction pattern; and this depends on

the brightness of a source, on its colour (on the wave-length of light in a case of a monochromatic source), and on the brightness and colour of the background. Considering the resolving power as a contact of the visible parts of two central spots, we see that the relation (9) gives that the part of the central spot perceptible to the eye is only about half a diameter of the first dark ring. Even if this be correct, it will be so only for quite a determined value of intensity and wave-length of light of a source, and cannot be applied *a priori* to all sources whatever their brightness and colour.

In a case of two point-sources, we can often consider two points as resolved though their central spots partly overlap each other.

If we assume the resolution as the least distance between two sources at which a distribution of illumination in the diffraction pattern due to both the sources is such that the difference between illumination at its maximum (on the meridional line) and that at central minimum is just perceptible to the eye, the expression (9) does not represent the conditions of resolution, as in this case the percentage difference of illumination is equal 26.5 (see below) and is much inferior to the limit of the contrast sensibility of the eye.

Different authors give different values for the contrast sensibility of the eye in a case of diffraction pattern. Thus Strehl \* gives 3-4 per cent., and found for this difference the least distance between two points just resolved to be  $D=3.2$ .

Wadsworth† in one of his papers on resolving power says:—"The first (resolving power) defines, as is well known, the power of an objective to 'resolve' or show as separate objects two or more close lines or points . . . , and the limit of resolution (angle between two points or fine lines that just appear separated) is represented by the well-known expression

$$a = m \frac{\lambda}{b},$$

where  $m$  is variable from unity for a rectangular aperture (of width  $b$ ) to about 1.1 for a circular aperture of diameter  $b$ ." We have for this case  $D=3.14$  for a rectangular aperture and  $D=3.55$  for a circular aperture. Wadsworth's

\* Strehl, *Zeit. für Instr.* xvi. p. 259 (1896). No details of this assumption are found in Strehl's paper.

† Wadsworth, 'Observatory,' xx. p. 333 etc.

data are taken from Lord Rayleigh's "Wave Theory," but they relate only to line sources which, in fact, have a first minimum at 3.14 and 3.55 for the rectangular and circular aperture respectively. Classen\* assumes the contrast sensibility of the eye in the case of diffraction pattern to be equal to 5 per cent, without any indication of the basis of this assumption. For this difference the distance between two point-sources will be  $D=3.3$ .

The contrast sensibility of the eye has in many cases been investigated in laboratory conditions: these investigations give the concordant results on the sensibility of the eye for different conditions of brightness. From König's results, recalculated by Branshard†, we see that the least difference of the field brightness just perceptible to the eye in the case of two adjacent fields is 0.017 for the field brightness equal to about 200 millilamberts. For a field brightness greater or less than this, the least difference just perceptible to the eye is greater than 0.017.

In many cases observers of double stars are able to resolve (even to measure a distance between) two stars, the distance between which expressed as  $D$  is much less than  $D=3.83$ , even than  $D=3.3$ .

We give here some data from several catalogues of double stars observed with different instruments. These data represent (for the given instrument) the least measured or estimated distances between two double stars' components of equal or nearly equal brightness. The distances obtained by measuring the two diameters of a complex oblong figure without resolving two components are not considered here.

Of course (7) cannot be strictly applied to observations of stars, as it refers to a monochromatic source of light and to a geometrically corrected object-glass. A determination of the resolving-power of an objective by astronomical observations is greatly influenced by atmospherical conditions, general absorption of atmosphere, brightness of a background; besides that the least distances at which two stars are resolved are taken from the measurement of these distances made with the same instrument, the resolving-power of which is to be found. For these reasons, the following values of  $D$  may be regarded as approximate ones. These values of  $D$  are calculated by means of (7),  $\lambda$  being taken equal to 0.00055 mm.

\* Classen, *Mathematische Optik*, p. 201.

† Branshard, *Phys. Review*, Feb. 1918.

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The values of the distances put in brackets are estimated values. In the square brackets are given the stellar magnitudes of the components. The data marked  $D_e$ ,  $\%$ , and  $D_e''$  are to be explained later.

			D".	D.	D <sub>e</sub> .	%.	D <sub>e</sub> ".
1. BURNHAM (36 inch).	1891 326		0''·07 ±	1·8	3·11	1·0	0''·12
(Publ. of Lick Obsy. ii.	389		·09	2·25	3·18	2·5	·13
p. 103.)	578		·09	2·25	3·18	2·5	·13
Σ 2367 [7·2-7·6].							
	1891 43		0''·09	2·25	3·18	2·5	0''·13
2. COMSTOCK (15·5 inch).							
(Publ. of the Washburn	1893 570		0''·21	2·2	3·17	2·5	0''·29
Obsy. x. pt. 1, p. 48.)	95 628		·23	2·4	3·21	3·0	·29
β 814 [8·5-8·5 (β)].	96 430		·21	2·2	3·17	2·5	·29
3. COMSTOCK (15·5 inch).							
(Ibid. p. 59.)	1895 805		0''·21	2·2	3·17	2·5	0''·29
Σ 2315 [7·8-0·0 Σ	96 665		·21	2·2	3·17	2·5	·29
Aeq-HΣ].							
4. O. STRUVE (15 inch).							
(Obs. de Poulkova, ix.	1847 45	(0''·22)	2·3	3·19	3·0	0''·30	
Suppl. p. 16.)	48 38	·25	2·6	3·27	5·0	·31	
Σ 1728 [6·0-6·0].	48 46	·26	2·7	3·30	6·0	·31	
42 Comæ Ber.							
5. O. STRUVE (15 inch).							
(Ibid. p. 39.)	1872 41	(0''·23)	2·4	3·21	3·5	0''·30	
OS 208 [5·5-6].	72 42	(·25)	2·6	3·27	5·0	·31	
φ Urs. Maj.							
6. BURNHAM (12 inch).							
(Publ. of Lick Obsy. ii.	1888 652	0''·24	2·0	3·14	2·0	0''·37	
p. 124.)	655	·23	1·9	3·12	1·5	·37	
OS 535 [7·7-5 (OS)].	714	·29	2·4	3·22	3·0	·38	
	733	...	...	...	...	...	
	1888 69	0''·25	2·1	3·15	2·0	0''·37	
7. W. STRUVE (4·9 inch).							
(Mesuræ Micr. p. 11.)	1827 26	0''·52	3·5	3·60	...	0''·53	
Σ 278 [8·4-8·7].	31 27	(·35)	2·4	3·21	3·0	·47	
	31 32	(·35)	2·4	3·21	3·0	·47	
	33 23	(·50)	3·4	3·56	...	·53	
	1830 77	0''·430	2·9	3·36	8·0	0''·50	

To investigate the question more closely, the values of  $I$  are calculated from (6) for the series of points varying in distance from the geometrical image of each point-source by tenths from  $-0·5$  to  $D+0·5$  for the different distances between the point-sources from  $D=2·9$  to  $D=5·1$ . The tables of all the values of  $I$  are rather long to be given here

in full; the values for the most interesting points (at the geometrical images, at the maxima and the central minima) are given in Table I. The values of  $I$  for some distances are plotted in Pl. II. fig. 1, where  $M_1$  and  $M_2$  represent the positions of maxima,  $O_1$  and  $O_2$  the positions of the geometrical images.

TABLE I.

D.	$I_0$	I max.	I min.	$\frac{I \text{ min.}}{I \text{ max.}} \cdot 100.$
2.9	1.0670	1.1528	...	...
3.0	1.0511	1.1073	1.1068	99.95
3.1	1.0377	1.0715	1.0607	99.0
3.2	1.0267	1.0463	1.0149	97.0
3.3	1.0179	1.0288	0.9692	94.2
3.4	1.0111	1.0167	0.9240	91.4
3.5	1.0062	1.0086	0.8794	87.2
3.6	1.0028	1.0037	0.8350	83.2
3.7	1.0008	1.0008	0.7912	79.0
3.8	1.0000	1.0000	0.7350	73.5
3.9		1.0002	0.7063	70.6
4.0		1.0011	0.6652	66.5
4.1		1.0025	0.6250	62.3
4.2		1.0044	0.5859	58.3
4.3		1.0064	0.5478	54.4
4.4		1.0085	0.5109	50.7
4.5		1.0105	0.4752	47.0
4.6		1.0124	0.4408	43.5
4.7		1.0141	0.4077	40.2
4.8		1.0155	0.3758	37.0
4.9		1.0165	0.3454	34.0
5.0		1.0172	0.3163	31.1
5.1		1.0175	0.2886	28.4

From the data of Table I. we distinguish three cases, namely:

- (1) The distances between two point-sources  $D > 3.83$ .
- (2) The distances from  $D = 3.83$  to  $D = 3.0$ .
- (3) The distances  $D < 3.0$ .

In the first case we have two maxima of illumination in the diffraction pattern. The positions of both the maxima correspond to the two geometrical images of the two sources, and vary in values depending on a distance between the sources according to variations of the value of  $1.0000 + I(D)$ :

For  $D = 3.83$  we have  $I = 1.0000$ ;

„  $D = 5.1$  „ „  $I = 1.0175$ ; etc.

D 2



The least difference between the illumination at maxima (at the geometrical images) and that at the point between them is 26.5 per cent. for the distance  $D=3.83$ . This difference is greater than necessary to be just perceptible to the eye. Two point-sources in this case are easily resolved as the general theory requires.

In the second case we have *two maxima also, but their positions do not correspond to the positions of the geometrical images*. For the distance  $D=3.83$  the displacement of the maxima does not as yet occur. As  $D$  decreases, the displacements of the maxima become more and more sensible. Both the maxima are displaced symmetrically towards the centre of the diffraction pattern.

The positions of the maxima for each given distance  $D$  may be determined as the roots of the equation

$$\frac{4J_1^2(z)}{z^2} + \frac{4J_1^2(D-z)}{(D-z)^2} = \max. \quad . \quad . \quad . \quad (10)$$

The displacements of the maxima for the different distances  $D$  are given in Table II. and Pl. II. fig. 2.

TABLE II.

D.	$\Delta z$ .	$2\Delta z$ .
3.8	0	0
3.7	$>0$	$>0$
3.6	0.05	0.1
3.5	0.1	0.2
3.4	0.2	0.4
3.3	0.3	0.6
3.2	0.4	0.8
3.1	0.7	1.4
3.0	1.1	2.2

We see that the displacements of the maxima of illumination increase very rapidly as the distance decreases.

In measuring (micrometrically) the distance between such very close point-sources we tend to set the cross wire certainly not at the geometrical images (which may be unknown) but at maxima of illumination which occur evidently on the meridional line in the diffraction pattern.

If the magnification of the instrument used would allow the measurements of the distance between two maxima in an image of two point-sources with such an accuracy that the errors of the measured distance would be much less than the displacement of maxima themselves, we must correct the measured distance to obtain the real one.

If we observe two close stars of equal brightness, their measured distance will be less than the real one, and *vice versa*, if we found from the measurements the distance between two point-sources to be less than  $D=3.83$  their real distance will be greater. To find the real distances we have to modify the Table II. so as to get the values of the real distances for the different measured distances.

TABLE III.

D.	$D_c$	D.	$D_c$	D.	$D_c$
0.8	3.00	1.9	3.12	2.9	3.36
0.9	3.01	2.0	3.14	3.0	3.39
1.0	3.02	2.1	3.15	3.1	3.43
1.1	3.03	2.2	3.17	3.2	3.47
1.2	3.04	2.3	3.19	3.3	3.51
1.3	3.05	2.4	3.21	3.4	3.56
1.4	3.06	2.5	3.23	3.5	3.60
1.5	3.07	2.6	3.27	3.6	3.67
1.6	3.08	2.7	3.30	3.7	3.73
1.7	3.10	2.8	3.33	3.8	3.80
1.8	3.11				

If the necessary accuracy as just determined cannot be obtained, the errors of the measured distance may be of the same order as the values of the displacement of maxima (particularly for the real distances near  $D=3.8$ ) and the corrections from the Tables II. and III. will not give the correct value of this distance. For the observed distance between the components of double stars given on p. 34 expressed in terms of  $D$  we find from the Table III. the corrected distances  $D_c$  and by (8) the corrected distances in arc seconds  $D_c''$ .

The values of the maxima of illumination in this case ( $3.83 > D > 3.0$ ) are given in the first table in column 3. We see that for these distances the maxima of illumination vary in value, increasing (as  $D$  decreases) from unity for  $D=3.83$  to about 1.1 for  $D=3.0$ .

The difference between the illumination at maxima (not at the geometrical images now) and that at the central point of the diffraction pattern decreases with the distance between the point-sources. The values of illumination at the centre of the diffraction pattern as referred to that at maxima assumed to be equal 100 are given in the fifth column of Table I. Pl. II. fig. 3 represents these variations of difference of illumination at the mentioned points.

This difference varies from 26.5 per cent. for  $D=3.83$  to 0.05 per cent. for  $D=3.0$ . These differences for the distances near  $D=3.0$  are hardly, if at all, perceptible to the eye.

In the third case ( $D < 3.0$ ) we have only one maximum at the point midway between two geometrical images: no central minimum exists in this case. As the difference between the illumination at its maximum and that at its central minimum in the case of  $D=3.0$  is only 0.05 per cent., this distance can be considered as the critical distance. In this case the difference between the illumination at its maximum and that at the geometrical images is 5 per cent. If we neglected the displacement of maxima and referred the illumination at the central point to the illumination at the geometrical images (instead of that at maximum) we should consider the distance  $D=3.16$  (instead of  $D=3.0$ ) as the critical distance, as for this case the difference of illumination is equal to about zero.

As  $D$  decreases, the maximum of illumination being always at the point midway between two geometrical images increases in value from 1.1073 for  $D=3.0$  to 2.0000 for  $D=0$  (i. e., two geometrical images coincide).

Thus this critical distance  $D=3.0$  must be considered as the absolute limit of resolution of two very close point-light sources of equal intensity.

In the table of the least measured distances between the components of double stars, we find under  $D$  the values less than  $D=3.3$  and even less than  $D=3.0$ . We have just seen that the last distance must be considered as the absolute limit of resolution. Having introduced the values of the displacements of the maxima and written for each  $D$  the corresponding corrected values  $D_c$ , we shall find that these distances are not less than  $D=3.15$  or 3.20. For these we have the difference between the illumination at its maximum and that at the central minimum equal to 2 or 3 per cent. respectively.

We have seen that the contrast sensibility of the eye in the most favourable conditions of brightness (200 ml.) does not exceed 1.7 per cent., and that only for the adjacent fields. In the case of a diffraction pattern we do not deal with two adjacent fields, and therefore the least difference of illumination just perceptible to the eye will differ from that limit value.

Therefore, if our assumption of the necessary accuracy of the measurements were fulfilled and thus the observed

distances could be converted by means of the data of Table III. into corrected ones, we might conclude from the observations of the double stars that the least difference between the illumination at its maximum and that at the central point in the diffraction pattern due to two very close point-sources of equal intensity, just perceptible to the eye, would be not greater than 2-2.5 per cent.

As we have said, the astronomical observations are greatly dependent on atmospherical conditions, and the real least difference of illumination for the case in question (diffraction pattern due to two very close point-sources) just perceptible to the eye may be less than that found from the observations of double stars.

In a case of two point-sources of unequal intensity, the illumination at a point in the diffraction pattern in the focal plane of an objective will be expressed by

$$I = \frac{4J_1^2(z)}{z^2} + n \frac{4J_1^2(D-z)}{(D-z)^2}, \quad . \quad . \quad . \quad (11)$$

where  $n$  is the ratio of intensities of two point-sources.

If we assume the intensity of a brighter point as unity,  $n$  will be less than unity and we have

$$I_2(z) = \frac{1}{n} I_1(z).$$

To represent the distribution of illumination along a meridional line, the values of  $I$  were calculated for the different  $D$  from  $D=3.0$  to  $D=5.1$ , and for the different  $n$  from  $n=0.9$  to  $n=0.01$ . These calculations were made as before, and all data are expressed in the illumination at the geometrical image of the brighter point being assumed to be equal to unity.

The whole table is too long to be given at length, and as before we give here but the final results (Table IV). In this table  $I_1$ ,  $I_m$ ,  $I_2$  denote the illumination at a first maximum, that at minimum on a meridional line, and at a second maximum. In the last column are found the percentage ratios of illumination at its minimum to that at a second maximum. The positions of the minima (their distance from the geometrical image of a fainter point) are added in brackets in column  $I_m$ . The values of the displacements of the maxima, if the latter exist, are given also in brackets in columns  $I_1$  and  $I_2$ .

TABLE IV.

D.	$n = 0.9.$				$n = 0.8.$			
	$I_r$	$I_m$	$I_x$		$I_r$	$I_m$	$I_x$	
3.2	1.0380(+0.35)	0.9529(1.0)	0.9533(+0.7)	99.92				98.41
3.3	1.0239(+0.2)	0.9131(1.3)	0.9316(+0.4)	98.0			0.8198(+0.3)	95.2
3.4	1.0140(+0.2)	0.8721(1.4)	0.9177(+0.25)	95.0		0.8068(1.1)	0.8039(+0.2)	91.4
3.5	1.0075(+0.1)	0.8309(1.6)	0.9083(+0.2)	91.4		0.7714(1.3)	0.8042(+0.1)	87.2
3.6	1.0030(+0.1)	0.7893(1.6)	0.9033(+0.1)	87.3		0.7350(1.4)	0.8009(+0.05)	82.7
3.7	1.0008	0.7484(1.7)	0.9008	83.1		0.6982(1.5)	0.8001	78.1
3.8	1.0000	0.7083(1.8)	0.9000	78.7		0.6614(1.6)	0.8011	73.6
3.9	1.0002	0.6694(1.9)	0.9002	74.4		0.6250(1.7)	0.8002	69.1
4.0	1.0010	0.6297(1.9)	0.9011	69.9		0.5894(1.8)	0.8026	64.6
4.1	1.0023	0.5922(1.95)	0.9025	65.6		0.5544(1.85)	0.8044(-0.05)	60.3
4.2	1.0039	0.5547(2.0)	0.9044	61.3		0.5198(1.9)	0.8065(-0.1)	56.1
4.3	1.0058	0.5190(2.1)	0.9064	57.3		0.4867(2.0)	0.8086(-0.1)	52.1
4.4	1.0076	0.4840(2.1)	0.9085	53.3		0.4540(2.0)	0.8186	48.3
4.5	1.0095	0.4503(2.2)	0.9105	49.5		0.4222(2.1)	0.8124	44.5
4.6	1.0112	0.4178(2.2)	0.9124	45.8		0.3922(2.2)	0.8141	41.0
4.7	1.0127	0.3862(2.3)	0.9141	42.2		0.3625(2.2)	0.8165	37.7
4.8	1.0139	0.3564(2.3)	0.9155	38.9		0.3343(2.3)	0.8172	34.4
4.9	1.0148	0.3272(2.4)	0.9165	35.7		0.3075(2.3)	0.8174	31.5
5.0	1.0154	0.3003(2.4)	0.9172	32.7		0.2815(2.4)		
5.1	1.0157	0.2735(2.5)	0.9175	29.8		0.2574(2.4)		

$n = 0.1,$

3.5	1.0053(+0.1)	0.7003(1.0)	0.7111(+0.25)	98.48	1.0017	0.5053(0.4)	0.6051(+0.2)	98.38
3.6	1.0050	0.6707(1.2)	0.7045(+0.1)	95.2	1.0005	0.5710(1.1)	0.6013(+0.1)	95.0
3.7	1.0046	0.6394(1.3)	0.7011(+0.1)	91.2	1.0000	0.5450(1.2)	0.6000	90.8
3.8	1.0040	0.6075(1.4)	0.7000	86.8	1.0001	0.5177(1.4)	0.6002	84.2
3.9	1.0031	0.5753(1.5)	0.7002	82.2	1.0007	0.4901(1.5)	0.6011(-0.1)	81.5
4.0	1.0018	0.5431(1.6)	0.7011	77.5	1.0015	0.4626(1.6)	0.6029(-0.1)	76.7
4.1	1.0015	0.5113(1.7)	0.7027(-0.1)	72.8	1.0026	0.4353(1.7)	0.6049(-0.1)	72.0
4.2	1.0030	0.4801(1.8)	0.7047(-0.1)	68.1	1.0038	0.4084(1.7)	0.6070(-0.1)	67.3
4.3	1.0045	0.4493(1.9)	0.7068(-0.1)	63.7	1.0051	0.3817(1.8)	0.6094(-0.1)	62.7
4.4	1.0059	0.4201(1.9)	0.7088(-0.1)	59.3	1.0063	0.3557(1.9)	0.6109(-0.1)	58.2
4.5	1.0074	0.3904(2.0)	0.7107(-0.1)	55.0	1.0074	0.3308(1.95)	0.6126(-0.05)	54.0
4.6	1.0087	0.3622(2.1)	0.7124(-0.05)	51.0	1.0085	0.3066(2.0)	0.6141	49.9
4.7	1.0099	0.3363(2.1)	0.7141	47.1	1.0093	0.2827(2.1)	0.6155	45.9
4.8	1.0108	0.3100(2.2)	0.7155	43.3	1.0099	0.2602(2.2)	0.6165	42.2
4.9	1.0115	0.2855(2.3)	0.7165	39.8	1.0103	0.2588(2.2)	0.6172	38.7
5.0	1.0120	0.2613(2.3)	0.7172	36.4	1.0105	0.2178(2.3)	0.6175	35.3
5.1	1.0122	0.2393(2.3)	0.7175	33.4				

$n = 0.4.$

3.7	1.0004	0.4919(0.7)	0.5016(+0.1)	98.07	1.0003	0.4022(0.4)	0.4022(+0.1)	100.0
3.8	1.0000	0.4732(1.0)	0.5000	94.6	1.0000	0.3911(0.7)	0.4000	97.8
3.9	1.0001	0.4519(1.2)	0.5002	90.3	1.0001	0.3765(0.9)	0.4002	94.1
4.0	1.0005	0.4295(1.3)	0.5013(-0.1)	85.7	1.0004	0.3603(1.1)	0.4015(-0.1)	89.7
4.1	1.0013	0.4067(1.4)	0.5032(-0.1)	80.8	1.0010	0.3429(1.2)	0.4034(-0.1)	85.0
4.2	1.0022	0.3857(1.5)	0.5052(-0.1)	76.0	1.0017	0.3250(1.3)	0.4054(-0.1)	80.2
4.3	1.0032	0.3607(1.6)	0.5073(-0.1)	71.1	1.0026	0.3088(1.4)	0.4079(-0.1)	75.2
4.4	1.0042	0.3380(1.75)	0.5093(-0.1)	66.4	1.0034	0.2884(1.5)	0.4098(-0.1)	70.4
4.5	1.0053	0.3157(1.8)	0.5112(-0.1)	61.4	1.0042	0.2700(1.6)	0.4114(-0.1)	65.6
4.6	1.0062	0.2923(1.8)	0.5129(-0.1)	57.0	1.0050	0.2518(1.7)	0.4131(-0.1)	61.0
4.7	1.0071	0.2727(1.9)	0.5143(-0.1)	53.0	1.0056	0.2340(1.8)	0.4145(-0.1)	56.5
4.8	1.0077	0.2519(2.0)	0.5155(-0.05)	48.9	1.0062	0.2167(1.9)	0.4155(-0.05)	52.2
4.9	1.0082	0.2321(2.1)	0.5165	44.9	1.0066	0.2001(2.0)	0.4164	48.1
5.0	1.0086	0.2133(2.2)	0.5172	41.2	1.0069	0.1841(2.0)	0.4172	44.1
5.1	1.0087	0.1947(2.2)	0.5175	37.6	1.0070	0.1704(2.1)	0.4175	40.8

$n = 0.5.$



$n = 0.05.$

D.	$I_p$	$I_m$	$I_p$	$I_m$	$I_p$	$I_m$	$I_p$
3.2					1.0007	0.0253(-0.7)	0.0282(-1.6)
3.3					1.0004	0.0238(-0.6)	0.0293(-1.5)
3.4					1.0003	0.0237(-0.5)	0.0305(-1.4)
3.5					1.0002	0.0242(-0.4)	0.0316(-1.3)
3.6					1.0001	0.0246(-0.3)	0.0327(-1.2)
3.7					1.0000	0.0249(-0.2)	0.0338(-1.1)
3.8					1.0000	0.0250(0)	0.0348(-1.0)
3.9					1.0000	0.0250(0.1)	0.0359(-1.0)
4.0					1.0000	0.0248(0.2)	0.0368(-0.9)
4.1					1.0000	0.0245(0.3)	0.0378(-0.9)
4.2					1.0001	0.0241(0.4)	0.0386(-0.7)
4.3					1.0002	0.0235(0.5)	0.0393(-0.6)
4.4					1.0002	0.0229(0.6)	0.0400(-0.6)
4.5					1.0003	0.0221(0.8)	0.0406(-0.5)
4.6					1.0003	0.0212(0.9)	0.0412(-0.4)
4.7					1.0004	0.0202(1.0)	0.0416(-0.3)
4.8					1.0004	0.0192(1.1)	0.0419(-0.25)
4.9					1.0004	0.0181(1.2)	0.0422(-0.2)
5.0					1.0004	0.0170(1.3)	0.0424(-0.1)
5.1					1.0004	0.0158(1.4)	0.0425

$n = 0.01.$

D.	$I_p$	$I_m$	$I_p$	$I_m$	$I_p$	$I_m$	$I_p$
3.0					1.0000	0.0038(0.2)	0.0253(-0.9)
3.1					1.0000	0.0037(0.3)	0.0257(-0.8)
3.2					1.0001	0.0034(0.5)	0.0260(-0.7)
3.3					1.0001	0.0032(0.6)	0.0263(-0.65)
3.4					1.0001	0.0030(0.7)	0.0266(-0.6)
3.5					1.0001	0.0028(0.8)	0.0269(-0.5)
3.6					1.0001	0.0025(0.9)	0.0271(-0.4)
3.7					1.0002	0.0028(1.0)	0.0273(-0.3)
3.8					1.0002	0.0027(1.1)	0.0274(-0.2)
3.9					1.0002	0.0029(1.2)	0.0275(-0.1)
4.0					1.0002	0.0035(1.3)	0.0275



In the diffraction pattern due to two point-sources of unequal intensity we have two maxima of illumination different in magnitude corresponding to two sources, and a minimum between them which is not in the centre of the diffraction pattern, but nearer to the geometrical image of a fainter source as  $n$  decreases, and even may lie on the other side of the geometrical image of this source.

As in the previous case, the displacements of the maxima occur at very small distances between the sources, but in the case of two sources of unequal intensity the displacements of the first (greater) maximum are less than those of the second (less) maximum. The influence of light of the fainter point on the position of maximum of illumination in the diffraction image of the brighter point is greater in the case of smaller differences of intensity of two point-sources; at  $n=0.6$  and less the fainter point does not influence the position of the first maximum, and for these differences of intensity ( $n < 0.7$ ) the first maximum is always at the geometrical image of the brighter point. The greatest displacement of the first maximum is  $+0.35$  for  $n=0.9$  and  $D=3.2$ .

As to the second maximum, its displacements resemble those for  $n=1.0$ , but in absolute value they are always less than those for the same distance. As  $n$  decreases the displacements of the second maximum decrease also and after reaching the value zero take the opposite sign (negative displacement), increase in value, and then again decrease to zero. As  $n$  becomes less the negative displacements of the second maximum occur for a greater number of values of  $D$ . For  $n=0.2$  and less the displacements of the second maximum are only negative.

In order to resolve two points of unequal intensity, the eye has to detect the difference in the illumination at its minimum on a meridional line and that at the second (less) maximum. The percentage ratios of the illumination at these points are given in the last column of Table IV.

The critical distances, as might be expected, are greater with decreasing  $n$ ; they are given in Table V.

TABLE V.

$n$ .	$D$ .	$n$ .	$D$ .
1.0	3.00	0.3	3.78
0.9	3.20	0.2	3.87
0.8	3.34	0.1	3.76
0.7	3.45	0.075	3.66
0.6	3.54	0.05	3.34
0.5	3.63	0.025	—
.	3.70	0.01	—

These values of  $D$  are obtained by the graphical extrapolation from the curves representing the last columns of Table IV.

It is necessary to note the fact that as  $n$  decreases, besides the influence of light of the central spot due to the brighter source, its first bright ring begins to influence the result curve of the distribution of illumination along a meridional line. This fact explains the decreasing of the critical distances for the  $n$  less than  $n=0.2$ , and therefore the decreasing of the distances necessary for a resolution of two sources. At the same time, for these values of  $n$  ( $<0.2$ ) the minimum of illumination on a meridional line is found, not between the geometrical images, but displaced away from the geometrical image of the fainter source (negative displacement); the second maximum is also displaced negatively.

When  $n$  has the value  $n=0.025$  and less—i. e., the illumination at the centre (geometrical image) of the diffraction pattern due to the fainter source is approximately the same as the illumination at the first bright ring due to the brighter source or less than this, the first bright ring overlaps the light of the central spot of the second source and we have no critical distance for these values of  $n$ .

It is evident that for the resolution of two point-sources of unequal intensity we need greater distances than for the case  $n=1.0$ . Thus if we consider, as is generally done, the distribution of illumination only along a meridional line, and assume 3 per cent. difference between the illumination at its second maximum and that at minimum as a practical limit for resolution, we should need the following distances for the different values of  $n$  :—

TABLE VI.

$n$ .	$D$ .	$n$ .	$D$ .
0.9	3.33	0.3	3.91
0.8	3.44	0.2	3.96
0.7	3.55	0.1	3.91
0.6	3.64	0.075	3.81
0.5	3.73	0.05	3.51
0.4	3.82		

In the case of two point-sources it is quite necessary to investigate the distribution of illumination not only along a meridional line but in a whole focal plane of an object-glass. For this purpose we must draw the lines

of equal illumination (isophotes) in a focal plane. In doing that, we can follow the method proposed by Nagaoka\*. This method essentially consists in the following:—We take two points at a given distance, and consider them as the geometrical images of two sources; then draw the lines of equal illumination (circles, in a case of point sources) for each point-source. The position of the lines of equal illumination we find from the curve representing the general expression (1a) drawn in a large scale. Thus we obtain:—

TABLE VII.

Illumination.	Z.	Illumination.	Z.
1.00	0.00	0.45	1.73
0.95	0.45	.40	1.84
.90	0.64	.35	1.96
.85	0.80	.30	2.08
.80	0.93	.25	2.21
.75	1.06	.20	2.36
.70	1.18	.15	2.53
.65	1.29	.10	2.74
.60	1.40	.05	3.00
.55	1.50	0.00	3.83
0.50	1.61		

At the points of intersection of any two circles the sum illumination will be the sum of two. Joining the points of equal sum illumination, we get the curves of equal illumination.

For the case of two point-sources of equal intensity, we give here, as examples, four figures for the distances  $D=3.83$ ,  $D=3.2$ ,  $D=3.0$ ,  $D=2.9$  (Pl. II. figs. 4, 5, 6, 7). In all these figures  $O_1$  and  $O_2$  represent two geometrical images of the sources,  $M_1$  and  $M_2$  the positions of the maxima of illumination. Scale of the original drawing: each centimetre corresponds to  $D=0.2$ .

From these figures we see that the isophotes corresponding to central minimum and those of a higher illumination intersect a meridional line at four points (two points being between two maxima, *i. e.* each maximum is surrounded by

\* Nagaoka, "Diffraction Phenomena in Focal Plane of a Telescope with circular aperture due to a Finite Source of Light," Journal of the College of Science, Imperial University, Tokio, vol. ix. p. 344 (1898), and Phil. Mag. xlv. p. 1 (1898).

these isophotes separately). The isophotes corresponding to a lower illumination surround two maxima together. The latter isophotes at their middle parts are convex (in respect to the central point in the diffraction pattern) with decreasing curvature as the distance between the sources increases. As the distance between the sources decreases, all isophotes become more and more of oval shape.

In the case of two *line* sources, we treat the conditions of their resolution only in respect to the least difference of illumination at its two maxima and that at point between them, just perceptible to the eye; but in this case the positions of the maxima and minima of illuminations are the straight lines: also by straight lines are represented all the other values of illumination.

A more complex case, as we see from Pl. II. figs. 4, 5, 6, 7, will be the case of two point-sources. The places of maxima of illumination in the diffraction pattern are two points. The places of all other values of illumination are the isophotes of a different form.

*It seems more than probable that in some cases the eye cannot detect the difference between the illumination at its maximum and that at its minimum on a meridional line, but detects the depression in the middle part of the compound figure—i.e., the depression in the middle parts of the isophote corresponding to the threshold sensibility of the eye.*

It is possible that owing to this fact nearly all laboratory determinations of the resolving power of objectives were made with pairs or series of line objects (Foucault, Rayleigh, Bigourdan, Nutting).

At the distances less than the critical distance all the isophotes intersect a meridional line only in two points; in their middle parts they become concave in respect to the central point and the observer sees a compound figure as "oblong" till the eye refuses to detect the difference of diameters of this oblong figure, then the latter appears as quite round.

For two points of unequal intensity the isophotes may be found in the following manner:—We take two points at a given distance, considering them as the geometrical images of two sources; draw for the brighter point the lines of equal illumination as before. To find the positions of the lines of equal illumination (radii of the corresponding circles) for the fainter source, the illumination considered is divided by  $n$  and with the result as an argument the corresponding

#### 48 *Diffraction Pattern in two very close Point-Light Sources.*

distance of each line of equal illumination from the geometrical image of the fainter point is found from the curve representing the general expression (I.a). Then, joining as before the points of intersection with equal sum illumination, we obtain the isophote in question.

We give here (Pl. II. figs. 8-15) as examples some cases of distribution of illumination in a focal plane for the following values of  $n$  and  $D$  :—

$n$ .	$D$ .	%.		$n$ .	$D$ .	%.
0.7	3.6	0.95		0.4	4.0	0.90
—	3.55	0.97		—	3.83	0.97
0.5	3.73	0.97		0.3	3.91	0.97
—	3.6	1.00		—	3.83	1.00

It may be seen from these figures that the isophotes corresponding to minimum of illumination (on a meridional line) and those for greater illumination intersect a meridional line in four points, dividing themselves into two separate branches; at the distances less than the critical one, all the isophotes intersect a meridional line only in two points. In this case the isophotes corresponding to illumination at the second maximum and those of less illumination surround two maxima together; the isophotes corresponding to illumination greater than that at second maximum surround only the first maximum. As the distances exceed the critical one for the corresponding value of  $n$ , the depression of isophotes, which approximately corresponds to the position of a minimum of illumination on a meridional line, becomes of greater curvature.

As in the previous case of two points of equal brightness, it is more than probable that for some cases the eye cannot detect the difference between illumination at its maximum and that at its minimum, but detects the central depression: *i. e.*, it cannot detect the contrast of illumination but detects a form of compound figure.

To determine the conditions of resolution of two luminous points by the eye, it is necessary to know the threshold sensibility of the eye for such a case of diffraction pattern: *i. e.*, to know the value of isophote corresponding to the threshold sensibility and to know the contrast sensibility of the eye for the same pattern.

The above given results show that it is very difficult, if not impossible, to take two point-sources as test objects

for the accurate determination of resolving power of an objective.

In all considerations about the mutual attraction or repulsion of stars' images the displacements of maxima of illumination in a diffraction pattern must be taken into account.

The distance between two very close stars (very close components of a double star), especially of equal brightness, must be corrected for this displacement of maxima of illumination.

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*IV. Physiological Limits to the Accuracy of Visual Observation and Measurement.* By H. HARTRIDGE\*.

CONTENTS.

- INTRODUCTION. Definition of the Limits to Accuracy which are considered in this paper.
- SECTION I. Acuity of the Eye for Grating and Double Star Test Objects.
- SECTION II. Acuity of the Eye for Contours under Various Conditions.
- SECTION III. Coincidence Methods of Measurement.
- SECTION IV. Interpolation Methods of Measurement.
- SECTION V. Contact Methods of Measurement.
- SECTION VI. Measurements of Depth and Distance.
- SECTION VII. Comparison Methods of Brightness and Colour Measurement.

INTRODUCTION.

*Definition of the Limits to Accuracy which are considered in this paper.*

**H**ITHERTO those factors which concern the accuracy of measurement that have been given much consideration are :—

1. The instrumental errors.
2. The mental bias of the observer.
3. The probable accuracy of the observations.

It would seem that there is a fourth factor which has not been fully recognized: namely, the effect of the physiological properties of the particular sense organ which is used as the connecting link between the instrument and the brain

\* Communicated by Sir J. J. Thomson, O.M., F.R.S.

of the observer. In this paper the sense of sight will alone be considered, partly because visual determinations are the most commonly used; partly because the eye has been found as the result of experience to give values which are constant and accurate; and partly because the physiological basis of the errors to which visual estimations are liable is more firmly established than it is in the case of the other special sensations, *e. g.* touch, taste, or smell.

## SECTION I.

### *Acuity of the Eye for Grating and Double Star Test Objects.*

As is well known, there are two features which tend to limit the accuracy with which a given optical instrument can perform. The first is known as the resolving power of the instrument. This defines the limit imposed by the optical performance of its lens system. The second is the fineness of grain of the screen or surface on which that image is formed. This concerns the type of sensitive surface which is being used for recording the optical image, whether it be, *e. g.* a photographic plate or the retina of the eye. In the case of vision, both these factors enter into the consideration of the accuracy with which measurements of different types can be performed by the eye. We can thus treat the eye from the point of view of an optical instrument, and from the wave theory of light we can calculate what separation there must be between the two objects in order that their images should be clearly defined on the sensitive surface of the retina. For example, Abbe's formula\* for the resolving

power of the microscope is  $r = \frac{f \times \lambda}{d}$ . Assuming  $f$  the focal length of the eye to equal 15 mm., and the mean diameter of the pupil " $d$ " to be 3 mm., and the mean wavelength of white light to be 5600  $\mu\mu$ , then  $r$  is found to equal 2.9  $\mu$ . This means that the images of two objects formed on the retina must be separated by this amount in order that they shall be resolved by the eye. Alternatively, if Fraunhofer's formula† for the resolving power of the telescope be employed, and if a suitable correction be introduced for the fact that the pupil is circular, as pointed out in a previous paper‡, a precisely similar formula is obtained and therefore

\* Abbé, *cf.* Conrady, *Journ. Roy. Micr. Soc.* p. 610 (1904) and p. 541 (1905).

† Fraunhofer, *cf.* *Airv, Camb. Phil. Trans.* p. 283 (1834).

‡ Hartridge, *Journ. Physiol.* lii. p. 231 (1918).

a similar value for the resolving power. I find that Everett and Porter \* have reached the same conclusion.

The histological limit to the resolving power of the eye is set by the distance separating two of the sensitive structures of the fovea. This is the part of the retina on which the images of objects are caused to fall when the greatest acuity of vision is required. The foveal cones as measured by a number of observers are summarized by Parsons † and are found to have diameters which vary between  $2.0\ \mu$  and  $5.4\ \mu$ , the probable mean value being  $3.2\ \mu$ . In order, therefore, for the images of two objects to be resolved separately by the eye, it is necessary that there should be at least one unstimulated cone between those two cones on which the images fall, that is, that the images must be separated by at least  $3.2\ \mu$ . This histological limit will be seen to agree fairly closely with that obtained on purely optical grounds for white light and a 3 mm. pupil.

The calculation of the optical limit of the resolving power of the eye was made on the supposition that the image was a perfect one, that is, that the lens system of the eye was free from all types of aberration and conformed as a perfect lens system accurately to deductions made from the wave theory of light. This supposition is, of course, far from being the case, for the eye is known to suffer from considerable amounts of chromatic difference of focus and chromatic difference of magnification. Spherical aberration also enters to a greater or less extent, and in certain cases also astigmatism must be taken into account as well. For these reasons, therefore, we should expect the optical performance of the eye to fall far short of the theoretical performance that might be expected of it on the supposition that it behaved like a perfectly corrected lens system. It is surprising, therefore, to find that the limit to the resolving power obtained by actual experiments with the eye is not very different from that which a theoretically perfect lens system would give. In support of this statement the following values may be given:—In the case of a double star the limit is  $4.5\ \mu$ . In the case of the grating test object it is  $3.6$ – $4.6\ \mu$ . In the case of the chequer test object it is  $4.6\ \mu$ . It will be seen that limits to the resolving power obtained by using test objects of various types, give limits which vary between  $3.6\ \mu$  and  $4.6\ \mu$ , these being the distances separating on the retina the geometrical images of the separate elements of the test objects in question. The mean of these values,

\* Everett and Porter, *Journ. Roy. Micro. Soc.* p. 405 (1907).

† Parsons, 'Colour Vision,' 1st edition, p. 9 (1915).



namely  $4.2 \mu$ , is not very different from that which would be expected either from the histological limit ( $3.2 \mu$ ) set by the diameter of the foveal cone, or the optical limit ( $2.9 \mu$ ) obtained for the eye regarding it as a perfect lens system. The problem as to how it is that the eye can behave in such a satisfactory way, in spite of the aberrations from which it is known to suffer, has already been considered in some detail in a previous paper\*. With regard to the effects of these aberrations on visual acuity, it is interesting to note that while Helmholtz† found no marked improvement in the visual acuity on compensating the chromatic aberration of the eye by means of a chromatically overcorrected focal flint and crown glass lens combination, Luckiesh‡, on the other hand, by using monochromatic light of considerable intensity obtained from a mercury vapour lamp, has obtained an improvement of roughly 15 per cent., on substituting pure green light for daylight. Of the two experiments I would regard Luckiesh's as the more reliable, because any additional optical system, particularly one containing a combination of highly curved lenses, must introduce other aberrations at the same time that it corrects the chromatic aberration in the eye. If this 15 per cent. improvement for monochromatic light be applied to the mean acuity value obtained for white light for the grating test object ( $4.2 \mu$ ), a value of  $3.6 \mu$  is obtained for the distance separating the centres of the images of the bright bars of the grating on the retina. This value for visual acuity by monochromatic light is, as might be expected, even closer to the limit set by the diameters of the cones ( $3.2 \mu$ ) and by diffraction ( $2.9 \mu$ ) than is the experimental value obtained for white light ( $4.2 \mu$ ). Two other factors of importance now require to be mentioned, namely, the effect of light intensity and pupil diameter. With regard to the former, it is generally agreed§ as the intensity of illumination of the test object increases, that an increase occurs in the acuity of the eye. Very marked is the increase at first, but with increase of light intensity a level is reached at which the acuity stays constant in spite of increased illumination. It is probable that beyond this point an increase in illumination is accompanied by decreased visual acuity, but further experiments are required to set this on a firm basis.

With regard to pupil diameter, it has been shown by

\* Hartridge, *Journ. Physiol.* lii. p. 231 (1918).

† Helmholtz, *Physiol. Optics*, 3rd edition, p. 157.

‡ Luckiesh, *Electrical World*, lviii. p. 450 (1911).

§ Parsons, *Roy. Lond. Ophth. Hosp. Report* xix. Part i. p. 109.

Lister\* and Cobb† that between certain limits (3 mm. and 5 mm. pupil diameter) visual acuity is not appreciably affected by the size of the pupil. Below 3 mm. both observers agree that acuity decreases with a decrease in pupil diameter. Above 5 mm. Cobb finds a decrease, while Lister finds practically the same value as at 3.3 mm. We may say then, so long as the eye be in a state of adaptation, no bright source of light be shining into it, and the pupil diameter be approximately 3 mm., that the maximum theoretical resolving power is very nearly attained.

It should, however, be carefully noted with regard to these experimental limits that they have been obtained as the result of tests carried out by skilled observers using prolonged observation under specially favourable conditions of lighting, etc., and that such good values would hardly ever be obtained even by keen-sighted observers for ordinary conditions of lighting in everyday life. We may say, then, that whereas the eye actually *can* under specially favourable conditions separate the images of objects when they are separated at the retina by  $3\mu$  to  $4\mu$ , it would greatly facilitate observations if they were not separated by less than, say, five times this value. It is necessary to point this out, because rules have been made by Helmholtz and others for the limiting useful magnifying power of the microscope when objectives of different numerical aperture are used‡. The use of very low magnifications has been advised on the ground that the eye is well capable of resolving such a fineness of structure. It should be pointed out, however, that although it is possible for the eye under almost ideal conditions to resolve a certain degree of fineness, yet it cannot do so unless these ideal conditions are attained, and, further, even under these circumstances the fatigue caused by the process of observation would be found to be very great. It should be noted, moreover, that the grating test object used for the determination of visual acuity consists of metal wires placed in front of a brightly-lit white surface. The bars are absolutely black, and the clear parts between quite bright. In the case of a periodic structure seen under the microscope this is not the case, because no matter how perfectly the instrument is corrected there is a certain

\* Lister, *cf.* Conrady, Journ. Roy. Micr. Soc. xxxii. p. 41 (1913).

† Cobb, Am. Journ. Physiol. xxix. p. 76 (1911), and Psychol. Review, xx. p. 425 (1913).

‡ Helmholtz, *Wissenschaftliche Abhandlungen*, vol. ii. p. 185, also *Pogg. Ann.* Jubelband, p. 569 (1874); Mallock, Nature, cix. p. 205 (1922).

amount of haze which makes the black parts milky. Aberrations, diffraction, reflected and scattered light all play their part in producing this haze. Further, it becomes relatively more and more marked as the structure becomes sufficiently fine to be reaching the limit to the resolving power of the instrument. When such images are formed on the retina the conditions are very different from those of the grating test object described above.

Experiment shows that as the difference between the amount of light reaching the eye from unit angle of the black and white parts of the image is lessened, the lower is the value of the visual acuity reached. The following values obtained by Aubert may be quoted as examples :—

Distances in $\mu$ between the centres of the retinal images of two white squares in order that they should be resolved.						
Size of square in $\mu$ .....	8.3	6.6	5.5	4.7	4.1	3.7
Distances for black ground .....	10.3	11.0	12.2	14.9	15.8	18.5
"    "    grey    "    .....	10.8	11.5	12.6	14.5	19.4	23.2

A similar decrease in visual acuity is obtained if under the same intensity of illumination grey letters on a white ground are substituted for black letters on a white ground. We conclude, then, that the image of a grating formed on the retina will require to be more highly magnified if the black parts of it are milky than is the case if a perfectly black and white image is formed. This is, then, an additional reason for requiring that the magnifying power used in such an instrument as the microscope should be several times greater than the theoretical minimum. Experiment will show roughly how much additional magnifying power is required. Thus the diatom *Pleurosigma angulatum*, well known to microscopists as an object for testing dry lenses of medium power, has a regular periodic structure the approximate distance between the elements of which is  $.58 \mu$ . This diatom placed 250 mm. from the eye would give images on the retina, the distances between which would be  $.035 \mu$ . But experiment shows that under ideal conditions the eye can resolve images  $4.2 \mu$  apart. A magnification of 120 diameters would be sufficient to cause the diatom markings to be this distance apart on the retina. This magnification should therefore, theoretically, be sufficient to make them visible. Now, since the formula for the resolving power of

the microscope is  $R = \frac{\lambda}{2 \text{ N.A.}}$ , then if white light is in use,

$\lambda = 5800$  A.U. approximately, and the N.A. required will be found to equal 0.5 almost exactly. Helmholtz's rule for the magnification, namely,  $264.5 \times \text{N.A.}$ , should therefore give a value of 133. That is roughly equal to the lowest possible value found above, namely 120. Now experiment shows that to the author's eye a magnification of 500 is near the mark. That is, Helmholtz's rule is approximately 4 times too small even for well-marked structures. The distance separating the images on the retina at the magnification of 500 required by the author's eye becomes  $17.5 \mu$ , which corresponds roughly to 5 times the diameter of a cone ( $3.2 \mu$ ). Therefore, if the geometrical images of two neighbouring parts of the periodic structure fall on two cones, there will be between these cones on the average three other cones which will correspond to the interval between the periodic structures.

It should be pointed out that this apparently high degree of magnification required by the author's eye is not due to abnormality in its refraction. Experiment shows\* his eye to be emmetropic with a visual acuity on Snellen's scale of 6/3, *i. e.* approximately twice that of Snellen's normal value. Persons with normal vision attaining 6/6 on Snellen's scale would therefore presumably require a higher magnification still, possibly 1000 (at 0.5 N.A.) for clear vision, and persons with abnormal sight a corresponding increase in the magnifying power. It is obvious from this consideration how erroneous is Helmholtz's estimate of 133 diameters for 0.5 N.A. (*i. e.*  $266 \times \text{N.A.}$ ). Gordon† reaches a similar conclusion.

Abbé's rule, *viz.*  $1000 \times \text{N.A.}$ , is nearer the mark, but this would certainly be too low for persons with normal sight under adverse conditions and for persons with abnormal sight under almost all conditions. A safer rule would be

$$2000 \times \text{N.A.}$$

Snellen's standard of visual acuity. A person with very good vision reaching Snellen's standard 6/3 would thus

require  $\frac{2000 \times \text{N.A.} \times 3}{6} = 1000 \times \text{N.A.}$  (which is equal to

Abbé's rule). A person with 6/9 vision would require  $3000 \times \text{N.A.}$ , and so on.

The conclusion to be drawn from this section is that optical, histological, and experimental considerations give to

\* Hartridge and Owen, Brit. Journ. Ophthalmology, Dec. 1922.

† Gordon, Journ. Roy. Micro. Soc. 1903, p. 418.

the eye a limiting resolving power of about  $4\mu$  at the retina, which value corresponds to slightly less than an angle at the eye of 1 minute of arc. It is not surprising, then, that this limit has been accepted for the purposes of calculating the numerical values of such properties of the eye as depth of focus. Helmholtz, for example, used this value for calculating what he considered to be the greatest attainable acuity of stereoscopic vision, and in consequence it was not generally recognized for many years after that experimental determinations of stereoscopic vision showed that the eye had a very much greater stereoscopic acuity than Helmholtz's values gave.

## SECTION II.

### *Acuity of the Eye for Contours under Various Conditions.*

Volkman appears to have been the first, in 1863, to point out that the acuity of the eye for contours can greatly exceed this value of  $4\mu$  displacement at the retina. He determined the smallest differences between the breadth of two white contours on a black ground that can be perceived by the eye. He found this difference stated in angular measure to be as little as 10 seconds of arc ( $0.73\mu$  at retina). Wulffing, in 1892, confirmed Volkman's observations and obtained values of 10–12 seconds of arc (mean =  $0.79\mu$  at retina). Hering, in 1899, showed that the edges of two rectangles did not appear in line with one another if there was a relative displacement of approximately 10 seconds of arc ( $0.73\mu$  at retina). I have recently confirmed Hering's value by means of a test object, consisting of a white circle some 5 cm. in diameter, having on one part of its circumference, 10 mm. in length, a small projection 2 mm. in width. This disk was mounted in front of a sheet of black paper, so that the projection could be rotated into different meridians about a pin passed through the centre. The projection was placed in different meridians by an assistant and was observed at increasing distances until the point was reached at which the projection was correctly observed eight times out of ten. The distance was found to be 130 feet, and at this distance the projection was calculated to subtend 11 seconds of arc at the eye of the observer ( $0.79\mu$  at retina). This confirms Hering's value almost exactly.

It is clear from these experiments that under certain

circumstances the acuity of the eye greatly exceeds  $4\mu$  displacement of the retinal image. Other observations on the accuracy with which contours can be set into coincidence confirm this view. For black lines on a white ground Bryan and Baker\* obtained an accuracy of 12 seconds of arc ( $0.87\mu$  on the retina), Hartridge obtained 8.5 seconds ( $0.62\mu$ ), Stratton† obtained 7 seconds ( $0.51\mu$ ). For white lines on a black ground Bryan and Baker obtained 9.5 seconds ( $0.69\mu$ ) and for a split line 8.0 seconds ( $0.58\mu$ ). It will be seen that the mean accuracy of the coincidence method is 9.3 seconds of arc, *i. e.* a displacement of the retinal image of  $0.67\mu$ .

It is found, further, that the acuity of stereoscopic vision provides yet another case of the accuracy of perception of contours. Thus the values below demonstrate a mean accuracy of 8.2 seconds of arc ( $0.57\mu$  on the retina). Pulfreich obtained a value of 10 seconds ( $0.7\mu$  on the retina), Heine obtained values varying between 6 and 13 seconds ( $0.4$ – $0.9\mu$ ), Bourdon obtained 5 seconds ( $0.35\mu$ ), Crawley 3 seconds ( $0.2\mu$ ), Breton‡, in the case of one skilled observer, found an accuracy of 4 seconds ( $0.28\mu$ ).

The visibility of single black contours on a white ground, or white contours on a black ground, provides another example. Aubert found a black line on a white ground visible to the eye when its edges subtended an angle of 6 seconds of arc. Smith Kastner obtained a value of 3.5. Hartridge, using bright brass wire, found 3.6, and Hartridge and Owen detected the direction taken by the arms of an L (bent out of black brass wire and suspended in front of a white background so that no shadow was cast) 8 times correctly in 10 trials when its edges subtended 3.1 seconds of arc at the eye. (A decrease in the angle of 5 per cent. resulted in 6 mistakes being made in 10 trials, showing how abruptly the limit is reached.) The mean value obtained is 4 seconds of arc ( $=0.29\mu$  at retina). In the case of white contours even lower values have been obtained, in fact any white object, no matter how narrow, is visible if the intensity of illumination is sufficiently great. Seidentopf's experiments on the ultra microscope have amply demonstrated the truth of this statement.

\* Bryan and Baker, *Proc. Opt. Convention*, 1912, p. 252.

† Stratton, *Psychol. Review*, vii. p. 429 (1900).

‡ Breton, *Journ. Roy. Navy Med. Section*, vi. p. 288 (1920).

These different mean values may for convenience be summarized in Table I. below.

TABLE I.

## Visual Acuity of the Eye for Contours.

	Seconds of Arc.	At Retina.
Visibility of a black contour on a bright ground .....	4.0	0.29 $\mu$
Appreciation of the position of a contour .....	10.5	0.76 $\mu$
Accuracy of coincidence of two contours .....	9.3	0.67 $\mu$
Acuity of stereoscopic vision .....	8.2	0.57 $\mu$
Mean ... ..	8.0	0.57 $\mu$

It will be seen that, taking 8.0 seconds as the mean accuracy of the above determination, the acuity of the eye where contours are concerned is roughly 7 times as great as that to be expected on the histological and optical grounds mentioned in Section I. We have therefore to consider how this accuracy is to be reconciled with the calculated resolving power of the eye, and the finite diameter of the cone. With regard to the former, Rayleigh \* gave the following formula for calculating the least width of black line for visibility when viewed against a self-luminous background :—

$$\frac{I_1 - I_0}{I_0} = \frac{2\alpha}{\pi}.$$

Perceptible percentage decrease of illumination multiplied by angle subtended at the eye by the lines of a grating for resolution to occur, equals angle subtended at eye by just visible black line. He showed, by experiment, that

$$\frac{2\alpha}{\pi} = \frac{1}{9.1}, \quad \therefore \quad \frac{I_1 - I_0}{I_0} = 11 \text{ per cent.}$$

Taking, similarly, objects illuminated by borrowed light, he showed that the formula is

$$\frac{I_1 - I_0}{I_0} = \frac{4a}{\pi}.$$

Perceptible percentage decrease of illumination multiplied by angle subtended at the eye by the lines of a grating for

\* Rayleigh, Journ. Roy. Micr. Soc. 1903, p. 474.

resolution to occur, equals angle subtended at eye by just visible black line.

If these  $\alpha$  values for self-luminous gratings and those illuminated by borrowed light be compared, it will be seen that a self-luminous grating is twice as easily resolved by the eye as one illuminated by borrowed light. But that the converse is the case for resolution of a single narrow black line. Since then the angle of the black line is roughly one-ninth that of the bars of the grating when both are on self-luminous grounds, the ratio must be one to thirty-six, when borrowed light is used. Now the experimental values for the grating test object thus illuminated have already been given above, the mean being 58 seconds of arc. A black line should therefore be visible when it subtends an angle one thirty-sixth of this, viz., 1.60 seconds of arc. But the lowest value given above was 3.1 seconds of arc, which is roughly twice Rayleigh's value. If the eye could be fully corrected for aberrations it is probable that a nearer value would be obtained to 1.60 seconds of arc. It is therefore clear that the performance of the eye does not exceed the limits calculated according to the diffraction theory of light.

We have now to consider how the limit apparently set by the diameter of the foveal cones comes to be exceeded:—

Since it has never been found possible to analyze experimentally the structure of the image formed on the retina, calculations based on the amounts of aberration present in the eye have to be depended on to give the intensity from point to point of that image. It is found in this way\* that the image, even of a point source, spreads itself over a large number of cones, but the intensity falling on the various cones will be very different. The two factors of principal importance are those mentioned in Section I., namely, diffraction and chromatic aberration†. I have also mentioned that increase in pupil diameter increases one but decreases the other, thus explaining how it is that the performance of the eye stays constant for pupils between 3 and 5 mm.. Calculation of the effects of these two factors on the image of a point source shows that the cone receiving the strongest stimulus is the one on which the centre of the pattern falls. The surrounding cones will be less strongly stimulated. A just noticeable white object will be that one which just stimulates the cone on which the centre of the image falls by an amount appreciably greater than that by

\* Hartridge, *Journ. Physiol.* lvii. p. 52 (1922).

† Hartridge, *Journ. Physiol.* lii. p. 176 (1918).



which it stimulates surrounding cones. A just noticeable black object will be that causing an appreciably less strong stimulus, and so on. For the movement of a contour to be perceived it must cause a cone on one side of the edge of the image to receive an appreciably stronger stimulus, and that on the other an appreciably weaker one, than before. The acuity of the eye will therefore depend less on the diameter of the cones than on its ability to perceive small changes in light intensity. If from various experimental values the amount of this just perceptible intensity difference be calculated the following values given in Table II. are obtained.

TABLE II.

Difference Threshold for Light Intensity required in different circumstances to account for the Acuity of the Eye.

Single black line on white ground .....	13 per cent.
Grating .....	20 „ „
Double line .....	12 „ „
Stereoscopic vision .....	12 „ „
Coincidence of two contours .....	22 „ „

It will be seen that on the average there must be a difference of 16 per cent. between the light intensity falling on one cone and that falling on its neighbour for that difference to be perceived. It should be noted that 16 per cent. is a threshold value very much higher than that found by experiment to be required for large groups of cones. Here 0.5 or 0.6 per cent. suffices. Thus it was found by Helmholtz that if there is a difference of more than one part in 165 in the illumination of two contiguous areas, the difference in illumination will be perceived. Further, it was found by the author that two absorption bands 100 A.U. wide can be set into coincidence with an error not greater than 1 A.U.\* Spectro-photometric measurements † show that 2 A.U. change of wave-length produces a 1 per cent. change in intensity in that part of the band where the density change is greatest. For a wave-length change of 1 A.U. to be perceived the retinal cones must be capable of observing a 0.5 per cent. change in intensity. Various factors affect the acuity of the eye for perceiving differences of intensity, one is the intensity of the light and the other the adaptation of the eye.

\* Hartridge, Proc. Roy. Soc. (Now in course of publication.)

† Hartridge, Journ. Physiol. xlv. p. 1 (1912).

It may be sufficient to summarize briefly the data concerning these factors as follows. If the light is not bright enough acuity is low, and probably if the light is too bright also acuity is low, *i. e.* there is between the two extremes an "optimum" brightness\*. With regard to adaptation, both incomplete and excessive adaptation appear to be disadvantages, *i. e.* there is an optimum for adaptation also.

### SECTION III.

#### *Linear Measurements by the Method of Coincidences.*

The various types of linear measurement which are employed in practice may be divided under two headings: those which use the principle of coincidence and those which use the principle of interpolation. As an example of the first, may be given the measurement of an object by a scale and vernier; as an example of the second, may be given the measurement of a length by means of an ordinary millimetre scale. The fractions of a millimetre are determined in the first method by means of a mechanical contrivance, and in the second method by means of imaginary subdivisions of the millimetre into tenths (and possibly into hundredths) by the eye. For convenience, these two types of measurement will be considered separately, *measurements by means of coincidences* being considered in this section.

Baker and Bryan† appear to have been the first to make direct measurements of the accuracy with which one line can be set into coincidence with another. They investigated three cases: (1) that of a black line on a white surface, (2) that of a white line on a black surface, and (3) that of a black line the centre part of which was adjustable, which may be referred to as a "split" line. Some of the values which they obtained have been given above in Section II. It will be seen that the average error of coincidence methods may be as low as  $0.5 \mu$  on the retina, *i. e.*  $8.3 \mu$  at 25 cm. from the eye.

It may at this point be interesting to consider what effect on accuracy the want of distinctness in the object will have; for example, absorption bands produced by pigments in the spectrum are found to have blurred outlines, which makes the measurement of the apparent boundaries of their edges a matter of very great difficulty. It is also difficult, owing to

\* Parsons, Roy. Lond. Ophth. Hosp. Reports, xix. Part i. p. 110.

† Bryan and Baker, Proc. Opt. Convention, 1912, p. 252.

the apparent considerable width of the band, to make accurate observations of the apparent centre of the absorption. When, however, the method of coincidences is employed, two such similar bands being set in line with one another, then it is found that the accuracy of measurement is very greatly increased. Thus, without the method of coincidences it is difficult to obtain an accuracy of less than 10 A.U., whereas with the method of coincidences it is found that an accuracy of 1 A.U. is not difficult to obtain\*. It is possible to convert this accuracy of 1 A.U. into values similar to those previously given, *i. e.* for the apparent accuracy of setting the images on the retina into coincidence. The value thus obtained is found to be  $0.76 \mu$ , which is but little greater than the accuracy of coincidences found by Bryan and Baker in the case of a sharply-defined black and white line. The reason for this apparently small difference between the values for sharp and blurred lines is that, in spite of the fact that a mathematically sharp line is measured on the one hand, and an absorption band with indefinite edges on the other, there is not so marked a difference in the two sets of images formed on the retina, because chromatic aberration and diffraction operate together to give to the image, both of a mathematically sharp line and an absorption band, an indefinite outline. Two important physiological factors operate together in both cases to reduce this apparent blurring in the retinal image, these are (a) the value of the absolute threshold of stimulation of the fovea for vision and (b) simultaneous contrast. With regard to the former, it is found by experiment that with a particular degree of adaptation of the retina there is a certain luminosity below which all objects appear black, and, alternatively, there is a certain threshold above which all objects appear white, but the effects of this upper threshold are not so important in the cases under consideration as the lower one. With regard to simultaneous contrast, it is found by experiment that the differences between the stimuli applied to any two neighbouring areas of the retina are greatly increased†, so that, for example, a grey surface on a black ground appears to become white, and so on. This factor must have very important effects on the appearance of what may be called gradients of intensity, that is, in cases like absorption bands in which there is a more or less gradual change of the intensity of illumination as one passes from one part of the image to another.

\* Hartridge, Proc. Roy. Soc. (Now in course of publication.)

† Hartridge, Journ. Physiol. l. p. 47 (1915).

Simultaneous contrast has the effect of making all such gradients appear very much steeper than they actually are, and, if there should be any discontinuities in the intensity curve, of accentuating such discontinuities so as to cause the areas bounding such discontinuities to appear still more different in intensity. It is these physiological factors which cause images on the retina to appear very much sharper than the theoretical distribution of intensity would lead one to suppose would be the case. These factors both reduce the blurring introduced into the retinal images by the aberrations in the lens system of the eye.

These same factors operate in the case of objects which themselves have blurred outlines, *e. g.* absorption bands, thus causing the accuracy with which two such bands can be placed in coincidence to be not very different from that obtainable in the case of objects the edges of which are sharp.

We can draw from the above considerations the following practical conclusions:—

The accuracy of the method of coincidences in the case of both sharp and blurred lines (absorption bands, etc.), is very great, being between 4 and 5 times the resolving power of the eye. The retinal images are adjusted into coincidence with an average error of less than  $0.8 \mu$ . This corresponds to an angle of 11 seconds, or to one-eightieth part of a millimetre at 250 mm. distance from the eye (*i. e.* the ordinary distance at which a scale or instrument would be placed for clear vision with the unaided eye). It should therefore be possible with an accurately constructed vernier to subdivide the millimetre into 80 parts. For this purpose 40 vernier lines per millimetre would be required at least, since apparent coincidence with two neighbouring lines would be construed as coincidence with a line not actually present but midway between the two. In practice, a  $\frac{1}{2}$  mm. scale is more suitable, and this will require but 20 vernier lines to obtain the full accuracy available. If the scale is viewed through a magnifying-glass a corresponding change in scale and vernier should be made. Further, any considerable break in a contour of regular form will be identified if it subtends at the eye an angle of more than 11 seconds. For example, through a telescope the satellites of one of the planets should be recognizable if the magnified image has an excrescence due to the satellite of more than 11 seconds. In the case of Venus, observers at Greenwich claimed to have seen the satellite which subtends an angle of 0.5 seconds of arc. This through a telescope of 1000 diameters should equal 50",

*i. e.* nearly 5 times the limiting value. There is little doubt that this satellite should be visible under good atmospheric conditions.

The coincidence method of measurement is liable to these types of error :—

- (a) Line thickness parallax.
- (b) Malfocus parallax.
- (c) Colour parallax.
- (d) Intensity and visual threshold parallax.

(a) *Line thickness parallax*.—In the case of indices which are attached to scales which lie side by side (*e. g.* scale and vernier), the accuracy is not so noticeably affected by line thickness as by a difference in thickness of the lines on the two scales. But even in the latter case the inaccuracy is small compared with that introduced into interpolation measurements by thick lines. (This will be considered later.)

(b) *Malfocus parallax*.—This is the error familiar to astronomers when two points under observation differ in position in the direction of the line of sight, or when two scales which are being placed in coincidence with one another are in different planes relative to the eye, *i. e.* one scale being nearer to the observer than the other scale. The avoidance of error due to these causes is, as a rule, simple, and practical details are well known. It should be noticed, however, that when both eyes are being used together during observations, it is usually one eye—called by oculists the master eye—by means of which the settings are made. It is known, however, that in certain individuals neither eye is master, but one eye is sometimes used for setting and, on other occasions, the other eye. This selection takes place without the observer being aware that any change is taking place. Errors may be introduced from this cause if the two scales do not lie in the same plane.

(c) *Colour parallax*.—Donders pointed out that the eye suffers from chromatic difference of magnification; Gullstrand estimates that violet images are 3 per cent. smaller than red ones. I have confirmed this value\*, and find that since the fovea is approximately 0.6 mm. to the temporal side of the optical centre of the retina, the foci for different coloured rays fall approximately along a straight line which

\* Hartridge, Journ. Physiol. lii. p. 176 (1918).

cuts the optic axis 11·5 mm. in front of the retina. The centres of the aberration disks formed on the retina by rays of different colour do not therefore coincide, but the blue disks fall relative to those of the yellow on the nasal side and red disks on the temporal. To this is due the phenomenon of chromatic stereoscopy described by Donders. The relative displacements of the centres of red and blue images on the retina is approximately 0·02 mm. That is an apparent displacement of about 0·3 mm. in a scale illuminated by monochromatic red light in reference to a scale lit by pure blue-violet light placed side by side with it at, say, 250 mm. distance from the eye of the observer. Two examples will be given :

Case 1. Suppose that first one eye and then the other be used for measurement, an error of 0·6 mm. might occur if the scales were illuminated by pure red and blue light respectively. Scales tinted red and blue would suffer smaller apparent relative displacements, because these would not reflect pure spectral colours differing greatly in refrangibility, but only mixed rays the mean refrangibility of which would be less. A smaller but still noticeable error should occur if, say, one scale be of gold and the other of silver (a common arrangement for a scale and its vernier).

Case 2. Suppose that the length of an object part blue and part red is being measured at 250 mm. from the eye ; then an error in the length of 0·3 mm. might result.

A number of other examples might be given, but errors of this nature can be avoided by avoiding coloured scales, making corresponding scales of similar metals, and measuring all coloured objects under monochromatic light of specified wave-length.

(d) *Intensity and visual threshold parallax.*—It has been found by experiment that the measurements of the mean wave-length of absorption bands are influenced

- (a) by the relative brightness of the illumination on the two sides of the bands (the band appears to be shifted towards the darker side), and
- (b) by the relative sensitiveness of the two parts of the retina on which the images of the edges fall\* (the band appears to be shifted to that side falling on the less sensitive half of the retina).

Since the image on the retina, even of a mathematical line,

\* Hartridge, Proc. Roy. Soc. B. lxxxvi. p. 128 (1913).  
*Phil. Mag.* S. 6. Vol. 46. No. 271. July 1923.

is a diffuse one, such a line must show similar though probably smaller shifts under the influence of these two factors. Suppose, for example, that a scale, consisting of black lines on a white ground, be discoloured by a localised dark stain, then if the edge of the stain happens to coincide with one of the lines, so that on one side of the line the ground is darker than it is on the other, then it would be expected that measurements made in reference to such a line would be inclined towards the darker side. These effects of intensity are probably negligible under ordinary circumstances. It would, however, appear best in practice to avoid any possible errors due to them by the use of clean scales.

The retinal factor is not so readily disposed of. It would seem best in practice either to examine the scales with their ends alternatively to the right and left, or to perform coincidence settings alternatively with the scales on which the determinations are being made and with another set as nearly like them as possible which can be examined with their ends alternatively to right and left.

The four cases just considered apply to the unaided eye, and, with suitable modification in the actual values of the errors, to the eye when looking through an optical instrument which has an exit pupil large in comparison with the pupil of the eye (*e. g.* a Galilean telescopic system or a magnifying-glass). When the exit pupil of the instrument is small in comparison with the pupil of the eye, it is found that three sources of error may occur in instruments which employ the coincidence method of measurement:—

- i. The first is well known, namely, when two objects to be set into coincidence do not lie approximately in the same plane, for if the eye suffers from spherical aberration (as is almost always the case), then a small side shift may be introduced, causing the one image to move in reference to the other when the eye is moved from side to side.
- ii. In instruments like the direct-vision spectroscope, a side shift may be introduced if the colours of the two images to be brought into coincidence are not the same; for example, in the direct-vision spectroscope it is usual to find a scale illuminated by white light in juxtaposition to the spectrum to be measured. Suppose, for example, that there are two lines in the spectrum under observation, one in the red and one in the violet. It will be found, owing to chromatic aberration, that if the eye was accurately

focussed for white light, rays from the violet part of the spectrum would be brought to a focus in front of the retina, whereas rays from the red end of the spectrum would be brought to a focus behind the retina. If the exit pupil of the instrument accurately coincided with the optical axis of the eye, no deflexion of these images relative to one another would result; but if the exit pupil of the instrument was to the left side of the optical axis of the eye, then it would be found that violet images would be displaced to the left and red images to the right, and *vice versa*. Supposing, then, the spectrum has its violet end on the left and its red end on the right, the difference in wave-length of the red and violet lines would appear to be exaggerated so that the violet line would appear to have too small a wave-length and the red line one that was too large. Alternatively, if the exit pupil of the instrument were to the right of the optic axis of the eye, the reverse conditions would hold good, and the converse would be the case. It was found in the case of a direct reading spectroscope by Zeiss that an error of approximately 50 Å.U. in the wave-length measurements of the violet helium line ( $\lambda=4713$ ) could be introduced by causing the rays from the instrument to pass through the extreme right or left-hand edge of the pupil.

- iii. In cases where an instrument with split field is being used, it is found that a relative shift of the two fields can occur if the exit pupils of the rays which have illuminated the two fields do not accurately coincide with one another, and if the eye suffers from spherical aberration (as is almost always the case). For example, supposing the upper of two fields to have its exit pupil to the right of the exit pupil in the lower of the two fields, and supposing that the exit pupil of the upper field passes through the periphery of the lens system of the eye (which is usually found to suffer from spherical under correction), then the images in the upper field will be found to be displaced to the right in relationship with images occurring in the lower field, and therefore errors will be introduced. This method is used in a large number of instruments, *e. g.* the chemical burette and the slide-rule.



## SECTION IV.

*Interpolation Methods of Measurement.*

This method depends on the visual subdivision of a space bounded by two lines. Suppose, for example, that the position of a line is being measured by means of a millimetre scale; the millimetre is subdivided by the eye into tenths and possibly hundredths, and the number of such tenths or hundredths added on to the whole number of millimetre divisions which the object is found to measure. The accuracy with which such a subdivision can be effected has been made the subject of measurement. In Table III. are given the mean values of ten measurements of certain distances; in the first column as adjusted by interpolation by the eye, and in the second column as actually measured by means of the vernier. In the third column are given the differences between these two methods of measurement.

TABLE III.

Showing Errors in Judging the Subdivisions of a 1 mm.  
Scale into Tenths at 25 cm. from the Eye.

By Eye.	By Vernier.	Error in $\mu$ on Scale.	Error in $\mu$ on the Retina.
0	0.000 $\pm 0.015$	$\pm 0.015$	$\pm 0.9$
+0.1	+0.196	+0.096	+5.8
+0.2	+0.286	+0.086	+5.2
+0.3	+0.373	+0.073	+4.4
+0.4	+0.462	+0.062	+3.7
+0.5	+0.535	+0.035	+2.1
+0.6	+0.635	+0.035	+2.1
+0.7	+0.666	-0.034	-2.1
+0.8	+0.727	-0.073	-4.4
+0.9	+0.829	-0.071	-4.3
+1.0	+1.000 $\pm 0.015$	$\pm 0.015$	$\pm 0.9$

An observation of this column will show that the whole reading in millimetres is very accurately judged, this depending on the coincidence of two lines; but the readings on other parts of the scale will be found to show considerable inaccuracy; *e.g.* the bisection of the space is judged inaccurately by 2  $\mu$ , the subdivision into the first tenth is judged inaccurately to 6  $\mu$ , and 4  $\mu$  for the two ends of the division respectively, other values giving errors which vary between

these two values. It will be seen, therefore, that there is considerable inaccuracy in making this type of measurement, an inaccuracy which was not less than  $30\ \mu$  at 25 cm. from the eye, and was in one case more than  $90\ \mu$ , whereas the corresponding errors found for coincidence measurement at 25 cm. from the eye are very much smaller, being about  $10\ \mu$ . This inaccuracy, which appears to be large everywhere and to increase as one of the lines is approached, seems to be due to a physiological factor, namely, that in subdividing a space bounded between two lines, it is not the space as measured from the centre of one line to the centre of the other line which is subdivided by judgment, but, for example, in the case of black lines the white area which extends from the edge of one black line to the edge of the other. This means that the area subjected to subdivision is not the whole area, but is the area from which the thickness of the lines has been subtracted. It would therefore be expected that this physiological error would be the greater the thicker the lines bounding the space, and I have a certain amount of evidence that that is the case. In the subdivision, therefore, of a scale by means of the method of interpolation, it is essential that the line thickness be kept as small as possible, and, further, if the personal error similar to that shown in Table IV. above be previously ascertained by the observer, a correction should be applied for the measurements made by the method of interpolation. The effects of colour if it be different in the two halves of the field, and of malfocus and want of coincidence in the exit pupils of the optic systems of the two fields, are similar to those considered above in the case of linear measurements.

## SECTION V.

### *Contact Methods of Measurement.*

In this method the images of two objects formed on the retina are gradually caused to approach until they just appear to come into contact with one another. For example, this method is employed when the size of the image of a microscopic object is being measured by means of the spider-line micrometer eyepiece. Another example is the case of the sextant, in which the bright image of the sun is brought into contact with the apparent edge of the horizon or with another image of the sun obtained by reflexion. Bryan and Baker\*, who made a very careful

\* Bryan and Baker, Proc. Opt. Convention, 1912, p. 252.

survey of the accuracy of contact measurements obtained with different forms of object, found that the accuracy depended largely on the test object. In certain cases, adjustment stopped short of contact, whereas in other cases there was an actual overlapping of the images before the contact appeared to be obtained. In general, it would seem from their determinations that black objects on a bright ground are not quite brought into contact, *i.e.* the measurements are too large; whereas bright objects on a black ground are caused to slightly overlap, *i.e.* the measurements are too small.

These constitute errors in the contact method of measurement, which are unquestionably due to the physiological properties of the retina.

Now, Nelson\* has published a formula by which the measurements of microscopic objects obtained by the contact method should be corrected so as to give the true dimensions of those objects. The formula he gives is:

$$\text{Correction in } \mu = \frac{\lambda}{5.47 \times \text{W.A.}},$$

where  $\lambda$  is the wave-length of the light and W.A. = working aperture of the objective.

The values given by it must be added to the experimental value in the case of black objects and subtracted from the experimental value in the case of bright ones.

If we applied such a correction to Bryan and Baker's results, we should find that the experimental value for the dimensions of a black object which are already too large owing to the fact that "contact" appears to be obtained when the spider-line and the black object are still separated by an interspace, would be made larger still, *i.e.* that Nelson's correction would add to the existing error, whereas in the case of bright objects on a black ground the converse would be the case.

Nelson's formula can be tested in another manner, with a 3 mm. pupil the W.A. of the eye is 0.1 N.A., and when this is inserted into Nelson's formula ( $\lambda$  being 5600 A.U. for white light) the value 1.025 is obtained as the correction. This is equal to a visual angle of 14 seconds of arc approximately. White objects should appear too large by this amount, while dark objects should appear too small. Aubert has given experimental values obtained by varying the

\* Nelson, Journ. Roy. Micr. Soc. 1903, p. 579.

distance between white lines on a black ground until the width of the interspace between the lines appeared equal to the width of the lines themselves. In this way he found that white lines subtending at the eye angles varying between 45 and 10 seconds of arc, appeared between 50 and 77 seconds of arc too large. Nelson's correction of 14 seconds of arc would be much too small. Aubert has also given values for black lines on a bright ground obtained in a similar way. He found that black lines subtending at the eye angles varying between 45 and 10 seconds of arc appeared too large by 34-41 seconds of arc. If Nelson's correction was applied in this case it would make the error larger and not smaller.

In most of the cases investigated by Bryan and Baker, it appears possible, from the values which they give, to estimate what the error will probably be for a particular individual with a particular type of test object; so that, this personal error being known, it should be possible to correct subsequent determinations. In other cases such correction would appear to be difficult if not impossible; for example, supposing the diameter of a highly-magnified object placed on the field of the microscope to be the subject of measurement by the spider-line micrometer. Then the edges of the image presented to the eye will appear to be surrounded by diffraction phenomena, which will vary with the working aperture of the optical system, and probably also with the colour of the light which is being used for illumination. Calculation of the distribution of intensity of light at the edge of the image will show that there is a gradient not unlike those met with in the case of absorption bands. The apparent edge, therefore, of an image with such a gradient of intensity of light will vary under similar conditions to those which have already been considered in the case of absorption bands. Suppose, for example, a black object on a bright ground to be under examination (*e.g.* a red-stained micro-organism), examined under direct blue-green illumination, the image will appear to increase in size as the brightness of the illumination is diminished; or as the working aperture of the lens system of the microscope is diminished (the intensity being kept constant); or, lastly, as the eye of the observer becomes fatigued, with a corresponding rise in the value of his visual threshold. Under these conditions, determinations by the contact method will be found to give values which are not only inaccurate themselves, but which are also, it would seem, incapable of correction.

A practical point may be mentioned in this connexion. It

is possible that a more accurate estimate of the true size of the object might be obtained if measurements of the edge were made, firstly, of the object when seen as a black image on a bright ground, and then by a change in the method of illumination, as a bright object on a black ground. In the one case, according to Bryan and Baker's experiments, the measurements will be too large, and in the other case they will be too small by the amount which the eye subtracts from, or adds to, the true diameter, owing to the apparent edge of the gradient being situated at a certain distance away from the actual commencement of the gradient. An average of these two determinations might be found to give the actual diameter of the image without great error from physiological causes. This subject requires further experimental investigation.

Another type of error occurs in contact measurements, that is when the image of one object actually obstructs the image of the other object when the two are caused to overlap one another. For example, in the Abbé\* apertometer it is necessary that the image of a cursor should be brought into contact with the edge of the restricting aperture of the objective lens system under measurement. Owing, however, to the fact that the image of the index lies in a plane below that occupied by the image of the aperture, the latter obstructs the former so that no apparent difference in the appearance to the eye results if the two are just mathematically in contact, or if there is a very considerable overlap. The eye, under these circumstances, has two alternatives before it—either to set the images so that it is seen that definite contact has just not occurred, or to set the images so that contact definitely has occurred, when, of course, there will be overlap by an extent which cannot be estimated by the eye. In either case there will be inaccuracy in the determinations. A method of avoiding this type of inaccuracy in the case of the apertometer has already been considered in a previous paper†. Briefly, the modification consists in such an alteration of the optical system that the indices lie between the restricting aperture under measurement and the eye of the observer. In the case of the apertometer this state of affairs is obtained by passing the illuminated beam in the reverse direction, *i. e.* in at the eyepiece of the microscope and out at the edge of the apertometer-plate to reach the eye of the observer.

\* Abbé, Journ. Roy. Micr. Soc. 1880, p. 20.

† Hartridge, Journ. Roy. Micr. Soc. 1918, p. 337.

## SECTION VI.

*Measurements of Depth and Distance.*

Three methods will be briefly referred to under this section :—

1. Monocular perception of depth by means of, *e. g.*, the micrometer microscope.
2. The monocular range-finder.
3. The binocular range-finder.

With regard to the first method, the usual procedure is to focus first one surface and then the other surface of the object whose depth is to be measured, and to ascertain the movement of the optical system that has been necessary in order to accomplish this. For example, in the case of a lens, lycopodium powder is sprinkled on the surfaces, and the grains on one surface and then the grains on the other surface are focussed in turn. This method of measurement is found to suffer from two errors, which are of a physiological nature :

- (a) The range of accommodation of the eye.
- (b) The depth of focus of the eye.

(a) *The range of accommodation of the eye.*—With regard to this, it will be seen that the accuracy of the determinations depends on the lower focal plane of the lens system preserving a constant relationship with the index of the scale of the instrument. But if a portion of this lens system, *e. g.* the crystalline lens of the eye, varies in its power, then the position of this plane must correspondingly alter. Suppose, for example, that the crystalline lens increases in power ; then it can readily be shown that the lower focal plane rises with respect to the rest of the instrument, and *vice versa*. To eliminate this error it is necessary that there should be placed in the field of the eyepiece a suitable object on which the eye can be focussed, *e. g.* a cross-wire. If, then, the observer suitably adjusts the accommodation of his eye so that this cross-wire is always accurately in focus, to a very large extent errors due to change in the degree of accommodation of the eye will have been eliminated—but not entirely, owing to the second factor, which will now be discussed in some detail.

(b) *The depth of focus of the eye.*—Since, as has been mentioned above, the sensitive surface of the eye consists

essentially of a number of sensitive elements of approximately known diameter, arranged compactly together, it can be readily calculated that the eye will have a certain depth of focus which will vary with the aperture of the pupil, the smaller the pupil the greater being the apparent depth. Two imaginary planes may therefore be drawn in front of the observer and parallel to his retina. Images of external objects falling between these two planes will appear to be sharply focussed to the eye. Corresponding to each of these planes, there will be two planes situated on either side of the lower focal plane of the whole lens system of his eye, and these two planes will tend to separate further from one another as the diameter of the emergent pupil of the optical system of his eye is decreased in diameter. So long as the surfaces under measurement lie between these two planes, they will appear to form sharply-focussed images on his retina, so that unless these two planes are situated so closely together that their distance of separation is small compared with the accuracy to which the measurements of depth are required, error will be introduced into the measurements effected by the method. It will be seen that this error can be made smaller by causing the exit pupil of the eye and of any instrument in use to increase in diameter. In fact, it is probably correct to say that the largest possible aperture should be employed in the optical system that will enable sufficiently sharply-focussed images to be formed on the retina. It will be found, further, that the error decreases for a given aperture as the magnifying power is increased, and therefore the highest magnification should be employed which will permit the required measurements of depth to be made.

To return, for example, to the case of the determination of the thickness of a lens, mentioned above, that objective should be selected for use in the microscope whose working distance will just permit the two surfaces of the lens to be focussed in turn; the objective should also have the largest aperture that can be obtained for this focal length; and that magnifying power should be used in the eyepiece which will enable sharply-focussed images to be formed on the retina. This eyepiece should be fitted with cross-wires in order to eliminate the effect of accommodation of the eye, mentioned in the previous paragraph.

*Monocular range-finders.*—Since this instrument employs the method of coincidences, the principal errors to which it is liable have already been considered under Section III.

It should be pointed out, however, that there are two particular errors to which the instrument would appear to be liable. Firstly, that due to colour-parallax, when the objects under measurement reflect a considerable amount of coloured light; and, secondly, aperture-parallax, due to the exit pupils of the two optical systems—that to the right-hand side and that to the left-hand side of the base-line—not exactly corresponding to one another. It has been pointed out above that if the eye suffers from optical aberration, this aperture-parallax may lead to a relative movement of the images in the two fields, which may produce errors in measurement.

*The Stereoscopic range-finder.*—It would seem that colour-parallax is the only serious error to which this particular instrument is liable on physiological grounds. Its avoidance could, it would seem, be effected by either introducing a suitable colour-filter which would limit the rays reaching the eye to a nearly monochromatic bundle, or by introducing a pair of prism elements having dispersion without deviation which would cause the images formed on the fovea to overlap one another accurately, and would thus eliminate the effects of chromatic difference of magnification of the retinal images.

## SECTION VII.

### *Comparison Methods of Colour and Intensity Measurement.*

Two methods of measurement are largely used at the present day for a variety of purposes :

- (a) Flicker photometry.
- (b) Comparison photometry.

With regard to the former, physiological variations have already been very thoroughly studied. With regard to the latter, it would seem that the conditions necessary for accuracy are not so well known. In colorimeters, polarimeters, spectro-photometers, and the like, three types of field are to be met with :

1. The circular field divided into two parts by a diagonal.
2. The circular field containing a smaller, centrally-placed subsidiary field (the so-called bull's-eye type of field).
3. The field divided into three parts by two parallel lines, so that the central strip forms one field and the two side strips form the other.



The errors to which measurements made with instruments which possess these three types of field are liable are, firstly, retinal after-images, and, secondly, retinal fatigue images. It is found that in all three types of field the attention appears to be concentrated on one particular part of the field, so that a definite pattern is always presented on the same parts of the retina. Supposing that at the commencement of measurement, one part of a field is always the brighter, and that adjustment be made by causing the two fields to become more and more alike until equality is reached, then that part of the retina corresponding to the brighter field will suffer to some extent from fatigue, and will also be occupied by what is known to physiologists as a negative after-image. Both these factors operate together to reduce, apparently, the sensitiveness of the retina, so that a brighter image has to be presented to this part of the retina than that required to stimulate the other portions on which the brighter image did not at first fall. The result will be that, when equality appears to have been obtained, the image which was initially the brighter is to some extent still the brighter, although it appears equal to the less bright part.

The bull's-eye type of field has, in addition to this error, a special error of its own. It is well known physiologically that the portion of the retina which corresponds approximately to the optical axis of the eye is the fovea. It is this part on which images are caused to fall by directing the eye towards them in order that the highest definition of visual acuity should be obtained. The fovea differs histologically from the more peripheral parts of the retina in having cones only, whereas in the more peripheral parts of the retina, rod retinal elements tend to predominate. It is well known that whereas the cones are used for the appreciation of colour, the rods are colour-blind, and therefore in the bull's-eye type of field the central area falls on the more colour-sensitive part and the annular field on the less colour-sensitive part of the retina. If, then, comparison of colours is being made, it will be readily seen that the bull's-eye type of field is specially objectionable. But, further, even if it is only intensity comparisons which are being made, the cones are known to function principally in day-time and the rods principally in night-time, and therefore, according as the general intensity of illumination of the fields is high or low, the centre or the periphery will appear to be relatively the brighter. In instruments allied to the spectro-photometer, a fourth type of field is occasionally met with\*, the eye focussing sharply

\* Hufner, *cf.* Milne, Proc. Opt. Convention, 1905, p. 178.

a narrow vertical slit in the plane of which a spectrum is produced. This spectrum is divided into two contiguous portions, one of which has passed through one limb of the instrument and the other through the other limb. Suitable adjustment is made so that these two halves appear to be alike in brightness, or, in certain cases, alike in colour. The disadvantages of this narrow field are that the line of junction of the two fields which are to be compared is so small compared with their total area, and it is usually found that the line of junction cannot be increased by making the slit wider without at the same time introducing an obvious difference of colour on the two sides of the field seen by the eye, which would, in its turn, have the effect of making comparison difficult.

The design and construction of colorimeters and spectrophotometers with fields which do not suffer from the errors that have been pointed out above, have been described in previous papers\*. The alternative type of field embodied in these instruments consists of a number of narrow strips having a very sharp line of separation between them, each alternate strip being illuminated by light from one or other limb of the instrument. Adjustment is made until the strips, regarded as a whole, appear to become alike in colour or intensity, so that their contours disappear, and the field appears to become uniform without any lines of separation.

With regard to measurements involving the determinations of shades of colour, it has been shown by Steindler and others that the sensitiveness of the eye to change of wavelength varies with the part of the spectrum under investigation, being greatest in the yellow-green and least in the red. Where mixed light, *e.g.* daylight, is concerned the eye appears to be most sensitive to variations about the neutral point. For example, the addition of a weak coloured light is more readily detected if it is added to a white light than if it be added to a coloured light of the same intensity as the white. This effect can, in practice, be frequently obtained by the use of colour-filters of suitable strength and of complementary colour to those under estimation. For example, a suitable piece of signal-green glass will be found to facilitate the change in the tint which occurs when vermilion oxy-haemoglobin changes to crimson reduced haemoglobin. Through the signal-green glass the oxy-haemoglobin appears orange, changing through neutral-grey to violet as it becomes reduced.

\* Hartridge, *Proc. Camb. Philo. Soc.* xix. p. 271 (1919); Hartridge, *Journ. Physiol.* l. p. 101 (1915).

*Summary.*

1. The limits to the accuracy of observation and measurement considered in this paper are those introduced by the imperfections of the eye.

2. Experiment shows that even under ideal conditions the centres of two lines or dots must subtend at the eye an angle of approximately 60 seconds of arc in order that they shall be seen as two. When the conditions are not ideal a much greater separation is required, even by normal-sighted people. People with defective vision require correspondingly greater separation.

3. Formulae have been published giving the limiting useful magnifying power for optical instruments of different aperture. Thus, in the case of the microscope, Helmholtz has given  $266 \times \text{N.A.}$  as the limit; while Abbé's formula is  $1000 \times \text{N.A.}$  Both are too low, even for persons with acute sight, and should be replaced by  $2000 \times \text{N.A.} \div \text{Snellen's standard of visual acuity for the observer}$ , this standard having been determined previously by experiment.

4. The visual acuity of the eye for the positions and movements of contours is nearly ten times greater than it is for the resolution of double points, and lines. This fact is made use of in mensuration.

5. The method of coincidences is found by experiment to give very accurate results. It has been found that the error at the eye is less than 10 seconds of arc ( $0.76 \mu$  error in the setting of the image on the retina).

6. Experiments by the author show that blurred lines, *e. g.*, absorption bands, are set into coincidence with approximately the same accuracy as are sharp lines. In this connexion it should be noted that, owing to diffraction and chromatic aberration in the eye, the images of sharp lines are diffuse, so that the retinal images in the case of blurred and sharp lines are not very different.

7. The coincidence method of measurement is found to be liable to a number of errors due to the physiology of the eye; these are:—(a) line thickness, (b) malfocus, (c) colour, (d) intensity of light, (e) visual threshold, (f) non-coincidence of exit pupils. The means of avoiding these errors is described.

8. The interpolation method of measurement used, *e. g.* in the chemical burette and the slide-rule, is much less accurate than the coincidence method. Otherwise the errors to which the method is liable are similar to those mentioned above in the case of the coincidence method.

9. The contact method of measurement used in the spider-line micrometer eyepiece is liable to error due (a) to irradiation, (b) to contrast. Bryan and Baker's experiments showed that the sizes of black objects are overestimated, while the sizes of white objects are underestimated. On the other hand, Nelson has given rules for the correction of the measurements made on objects under different methods of illumination; it is found, however, that when the correction is applied it tends to make the error larger. Further work is required to elucidate this problem.

10. Measurements of depth and distance are, in the case of monocular methods, liable to two errors: (a) due to the accommodation of the eye, (b) due to the depth of focus of the eye. The means of avoiding these errors is described. The errors to which monocular and binocular range-finders are liable are considered, and deductions drawn as to the relative accuracy of the two instruments.

11. The methods used in measuring colour and intensity are described. The form of the "fields" used in such instruments is criticized. An alternative type of field is suggested by which more accurate determinations may be made. For colorimetric work the use of complementary illumination is suggested.

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*V. On Images obtained by means of a Semi-infinite Obstacle.*

By SATYENDRA RAY, M.Sc. (Allahabad) \*.

[Plate III.]

THE object of the present paper is to point out that if light is passed through a number of parallel slits, which therefore serve as independent sources, a straight edge held parallel to the lines will produce on a screen an image of the slits. The image is inverted, as can be easily seen by stopping any particular slit with a thin rod.

The image is best described as being very similar to the diffraction image that would be expected by placing a slit just outside the straight edge. This can be demonstrated by bringing another edge from the opposite side. In fact a little attention will show that the second edge carries with it its own image of the pattern, and that the slit forms the clearest image when the images separately due to the two edges suitably overlap. The above phenomenon is the analogue, at any rate for linear objects, of the effects

\* Communicated by Prof. A. W. Porter, F.R.S.

# 80 *Images obtained by means of a Semi-infinite Obstacle.*

produced by a pin-hole camera, or again, of the images obtained by means of an opaque disk shown by Prof. A. W. Porter\*.

Variation of the distances of the object and the screen makes the size of the image vary according to the pin-hole camera law. If the light is passed through Wratten filters no perceptible change in the image is noticed. The image is produced by a cylindrical edge equally well, a brass tube or the wall of a glass bottle serving the purpose of an edge.

We can explain the phenomenon easily if we take into account only the first maximum of the diffraction fringes due to each source and neglect all the rest. That we are justified in doing this is seen by taking a photograph of the image produced by a single slit source. In this case the first diffraction band is by far the most prominent, as can be seen in fig. 1 (Pl. III.), which gives us the fringes corresponding to a thin slit source less than  $1/5$  mm. in width. As the position of the different maxima from the edge of the geometrical shadow due to a slit is given by

$$x = \sqrt{\frac{q(p+q)}{p}} (2n+1)\lambda,$$

where  $p$  and  $q$  are distances of the slit and screen from the edge, and as the image follows the pin-hole camera law

$$x = a \frac{q}{p},$$

maxima other than the first for each slit can only tend to make the pin-hole camera effect confused.

In figs. 2 and 3 (Pl. III.), we have the photographs of the images formed by a razor blade held parallel to the wires of a wire grating at a distance of 50 cm. from it, the distances of the screen from the edge being 100 and 200 cm. respectively. The four wires and the five slits of the grating may be seen in the image.

The writer stumbled upon the experiment accidentally at Meerut College, India in 1911, by sunlight, passing through a split bamboo screen, forming such an image by the edge of a book. The photographs reproduced here were taken at University College, London. I am grateful to Prof. A. W. Porter for his kind interest in the experiment and for guidance.

University College, London.  
24th Nov., 1922.

\* Phil. Mag. xxvii. p. 673 (1914).

VI. *The Recording Ultramicrometer: its Principles and Application.* By JOHN J. DOWLING, M.A., F.Inst.P., M.R.I.A.\*

**I**N a short paper before the Royal Dublin Society †, I gave a preliminary account of the employment of an oscillating valve circuit as an ultramicrometer. I now propose giving a fuller account of the principles of the device, together with particulars of some further tests of the apparatus ‡.

The ultramicrometer was a natural development of an electric valve method I described a short time previously § for measuring small-capacity variations. This latter method required an external source of high-frequency alternating current, and it occurred to me to try to incorporate in the apparatus itself the necessary elements of an oscillation circuit so as to make it self-contained. It will, of course, be understood that an apparatus which records small capacity variations will be immediately suitable for measuring minute movements, inasmuch as the capacity of a condenser varies with the separation of the plates.

A principle of a completely different kind was employed in the ultramicrometer device described by Whiddington ||. This was an application of the well-known "heterodyne" method first described a year earlier by American workers ¶. The characteristic "heterodyne note," due to the beating of the electric oscillations in two oscillating circuits nearly in tune, varies if the capacity of one of these circuits is altered slightly. English writers have occasionally confused Whiddington's apparatus with that here dealt with. There is nothing in common between them beyond the fact that radio apparatus is employed in both. The complexity of Whiddington's heterodyne method, due to the employment of *at least* two oscillating circuits; the fact that only acoustic effects are observed, which, in practice, involves some strain

\* Communicated by the Author.

† Proc. Roy. Dubl. Soc. vol. xvi. p. 18 (March 1921).

‡ Other accounts were published in 'Engineering,' Sept. 8th, 1921; 'Scientific American,' Feb. 1922; *Die Umschau*, March 1923; besides many summaries of these. The apparatus was exhibited at the British Association at its Edinburgh meeting, 1921.

§ Proc. Roy. Dubl. Soc. vol. xvi. p. 17 (Feb. 1921).

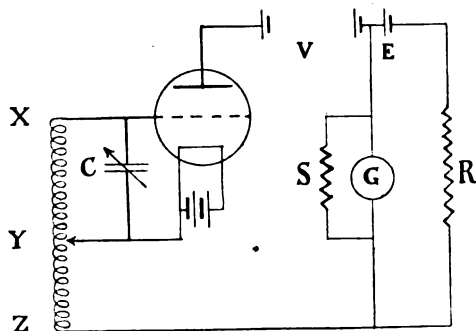
|| Whiddington, *Phil. Mag.* vol. xl. (Nov. 1921).

¶ Hyslop & Carman, *American Phys. Soc.* Dec. 1912; *Phys. Rev.* vol. xv. p. 243 (1920).

on the observer \*; and the fact that the mean separation between the condenser plates (a small and difficultly measurable quantity) has to be determined—all render the “heterodyne” method unsatisfactory. I should like to testify, however, to the ingenuity which Whiddington has shown in the application of the method.

A simple form of oscillating circuit is shown in fig. 1, in which, for the present, we shall imagine S, G, R, and E to be replaced by a milliammeter. The condenser C is of the variable sector type, and the coil XYZ consists of about 150 turns of bare copper wire wound in a helix on a wooden frame of about 6 in. square section and 2 feet (60 cm.) long.

Fig. 1.



The valve may be an ordinary “R-type” valve, with a 4-volt filament battery, and the anode battery V is of 50 volts. For certain positions of the filament connexion Y on the coil, the circuit will oscillate, and it is found that the milliammeter in the anode circuit then shows an increased reading. This effect is much greater when the grid potential is such that the valve is operating near the lower (or upper) bend of its characteristic before oscillations begin. For too small, or too large, values of the capacity the oscillations usually cease, and between these values the milliammeter readings vary with the capacity.

The curves in fig. 2 show some observations originally taken in order to get some idea of the conditions obtaining. The condenser then available was of limited range (100 to 1200  $\mu\mu$  farads), and it was not possible to trace the complete range of oscillation for any one fixed position of Y. A series of curves are therefore given, the number on each being the

\* Cf. Carman & Lorance, Phys. Rev. vol. xx. p. 715 (Dec. 1922).

length in cms. in the part XY included in the oscillation circuit ("tuned grid circuit"). A detailed discussion of these curves is, however, beside our purpose. It is sufficient to notice that many of them are quite steep in gradient, and, what is much more important, several (such as those for 40 cm. and 44 cm.) have a pronounced hyperbolic form over a good part of the range shown. In many places we find a variation of 1 milliampere per 100 micro-microfarads, or, roughly, 10 *micro-amperes per centimetre variation of capacity*.

Let us, now, consider a condenser formed of two circular disks of radius  $r$  cm. and  $x$  cm. apart. In electrostatic units,

$$C = \frac{r^2}{4x};$$

hence

$$\frac{dC}{dx} = -\frac{C}{x}. \quad \dots \dots \dots (1)$$

Assume  $r = 5$  cm.,  $x = 0.025$  cm.; so that  $C = 250$  cm. and  $\frac{dC}{dx} = -10,000$ . Thus a decrease of 1 cm. in the capacity accompanies a separation of the plates of only  $1/10,000$  cm.

At the point 277  $\mu\mu$  f. (*i. e.* 250 cm. capacity e.s.u.) on the curve 40 (fig. 2) the slope is roughly 8 micro-amperes per cm. capacity. Therefore, if the condenser just considered were employed in this case, we should expect to obtain an anode current *variation* of 8 micro-amperes for a relative displacement of the condenser plates of  $1/10,000$  cm.

It must however be noticed that the plate current, which undergoes this variation, is already of a strength of over 3 milliamperes.

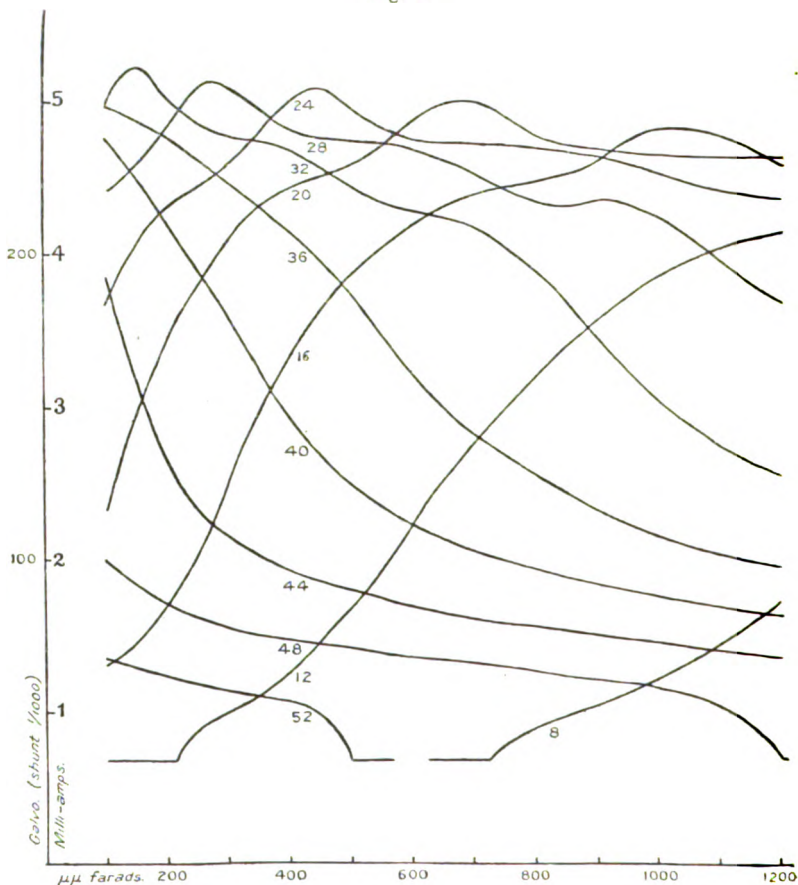
The milliammeter, which we have so far supposed to have been used to measure the anode current, is incapable of registering this small variation, and a special device is substituted, as shown in fig. 1, to enable this to be done.

A resistance  $R$  and an extra battery  $E$  are connected in series with the anode battery  $V$ , and the value of  $R$  is adjusted so that the anode current through it produces a drop of potential equal to the P.D. maintained by  $E$ . There will then, clearly, be no difference of potential between the points to which the galvanometer  $G$  is shown connected. If, however, a change takes place in the anode current, this no longer obtains, and the *excess* (or *defect*) current divides between  $G$  and  $RE$  according to the laws of parallel



circuits. In other terms, the galvanometer is completely shunted for a certain "zero" value of the current, but not

Fig. 2.



for other values: hence the name "zero shunt," by which I call the device. The theory is as follows:—

Let  $i$  be the "zero" anode current for which we desire the galvanometer to show no deflexion,  $g$  the resistance of the galvanometer circuit,  $R$  and  $E$  the resistance and e.m.f. constituting the "zero shunt." Then

$$iR = E. \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Suppose  $i$  increase to  $i + \Delta$ , and let  $a$ ,  $b$  be the currents

through the galvanometer circuit and  $R$  respectively :

$$ag = Rb - E, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$i + \Delta = a + b. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Thus  $R(i + \Delta) = Ra + Rb = Ra + ag + E$  ;

$$\therefore R\Delta = (R + g)a.$$

Hence

$$a = \frac{R}{R + g} \cdot \Delta, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

which expresses the fact stated above. It will be clear that  $R$  and  $E$  can have any values satisfying (2), but if  $R$  is made large compared with  $g$ , practically the *whole* variation  $\Delta$  of the anode current passes through the galvanometer.

Returning to the consideration of the "capacity current" curves, it will now be evident that the complete arrangement shown in fig. 1 may be extraordinarily sensitive to changes in capacity if a moderately sensitive galvanometer is employed. Suppose the galvanometer used gives a deflexion of 100 scale-divisions per micro-ampere—an ordinary laboratory value. Reverting to our previous numerical example, 1/10,000 cm. displacement of the condenser plate caused an anode current variation (" $\Delta$ ") of 8 micro-amperes. With a high-resistance zero shunt the galvanometer in question should show 800 scale-divisions; that is to say, *one* scale-division represents a plate movement of 1/8,000,000 cm. This enormous sensitivity might seemingly be exceeded by selecting curves of steeper gradient; but in doing so there are other conditions which, in practice, it is very important to keep in view. By deriving an expression for the sensitivity of the apparatus we shall arrive at these.

Let us define the micrometric sensitivity ( $M$ ) of the apparatus as the displacement of the condenser plates necessary to produce a deflexion of one galvanometer scale-division. Let

$a$  = galvanometer current (amperes),

$G$  = galvanometer constant =  $a/D$ ,

$D$  = galvanometer deflexion due to current  $a$ ,

$$f = \frac{a}{\Delta} = \frac{R}{R + g} \quad (\text{as above, equation (5)}),$$

$\Delta = di$ , where  $i$  = anode current,

$s$  = slope of "current-capacity" curve (fig. 2) =  $\pm \frac{di}{dC}$ ,

$C$  = (variable) capacity in e.s.u. =  $A/4\pi x$ ,

$x$  = separation of condenser plates.

Then

$$G \frac{dD}{dx} = \frac{da}{dx} = f \cdot \frac{di}{dx} = f \cdot \frac{di}{dC} \cdot \frac{dC}{dx} = -\frac{f \cdot s \cdot A}{4\pi x^2} = -\frac{f \cdot s \cdot C}{x} \quad (6)$$

Hence

$$M = \frac{dx}{dD} = -\frac{Gx}{f \cdot s \cdot C} = -\frac{4\pi G}{f \cdot s \cdot A} x^2 \quad (7)$$

An important deduction may now be made. If the sensitivity remains at a constant value  $S$  over an extended range of displacement of the condenser plates,

$$M = \text{constant} = -\frac{4\pi G}{fsA} x^2 = -\frac{AG}{4\pi f \cdot C^2 s}.$$

Thus

$$\pm C^2 \frac{di}{dC} = C^2 s = -\frac{GA}{4\pi f M} = \text{constant} \quad (8)$$

Integrating,

$$\frac{GA}{4\pi f M} \cdot \frac{1}{C} = j \pm i, \quad (9)$$

where  $j$  is a constant, and either the  $+$  or  $-$  sign may be taken.

Both these forms represent hyperbolas, and I have already pointed out that many of the " $C_i$ " curves of fig. 2 approximate over large parts of their contours to this type. This is especially so on the parts where  $s$  is negative, as, for example, the greater part of curve 40, including the region chosen for our previous calculation. By adjusting the apparatus to function in such a region, a wide range of practically constant sensitivity is available. This facilitates very considerably the practical application of the micrometer device. For, by working within this range, it is not necessary to know the actual *total* separation ( $x$ ) of the condenser plates; and indeed one can generally judge the right distance by the eye. Furthermore, the actual calibration of the apparatus may be simply done by giving one of the plates a predetermined minute displacement, and we are justified in assuming that the value of  $s$  so obtained is still applicable, even though the plates are subsequently moved very far from the point of calibration (provided that the capacity remains within the "hyperbolic" range).

Assuming the apparatus working within this "hyperbolic" range, we then have  $C^2 s$  constant (eq. 8) and (7) the sensitivity

$$M = \frac{Gx}{fsC} \propto \frac{GxC}{f} \propto \frac{G \cdot A}{f} \quad (10)$$

The proportionalities refer to a particular chosen coil adjustment, but the equality on the left is applicable generally. With a given adjustment of the coils, therefore, the sensitivity is *proportional to the area* of the condenser plates employed and to the sensitivity of the galvanometer. The factor  $f$  is in practice nearly unity. From our definitions of  $M$  and  $G$  a great sensitivity means a very small numerical value, so that (10) indicates that higher sensitivity is obtainable with condenser plates of small diameter very close together.

Hitherto we have considered the "current-capacity" curves from the point of view regarding the suitability of the apparatus as a micrometer device. On some such curves there are sections where the slope is sensibly uniform—*i. e.* where a *linear* relation exists between the anode current and the capacity. Professor Carman\*, of Illinois, has made use of this feature of the ultramicrometer circuit to measure minute capacity differences in connexion with his work on the dielectric constant of gases.

Besides these two "useful" portions, many of the curves show humps and shoulders, and frequently two distinct maxima. Some experiments have been carried out to determine, if not the origin of these irregularities, at least how best to modify the circuits so as to reduce or eliminate them. Incidentally, some experimental confirmation of the theory of the functioning of the circuit has been forthcoming. We now proceed to deal briefly with these questions.

So far the apparatus under consideration has been a simple "tuned grid" circuit with a rather large coil. I have found that much better results are obtainable with this same circuit, if a shorter coil of rather wider diameter is employed (20 cm. long; 20 cm. diameter: 42 turns No. 22 copper). With about 15 turns in oscillating grid circuit, a very large range of high uniform sensitivity is obtained.

However, the single coil, if it is to permit of "coupling" adjustment by alteration of the connexion  $Y$ , has to be wound with bare wire and the turns spaced. Naturally it is not compact. A much more satisfactory arrangement is obtained by using two "pancake" or "basket" coils. These can be mounted so that the coupling is adjustable by transverse or axial displacement of one of the coils.

\* Carman, *loc. cit.*

I have generally employed a pair of coils of 10 cm. diameter, wound with about 150 turns No. 28 or No. 36 D.S.C. or enamelled copper wire. A variometer can also be used. There are, in all, four simple circuits which serve almost equally well when properly set up and adjusted :—The “tuned grid” (fig. 1), already dealt with : “tuned plate” ; “Hartley” (fig. 3) ; “modified Meissner” (fig. 4). The last-named is not so simple as the others, requiring a third

Fig. 3.

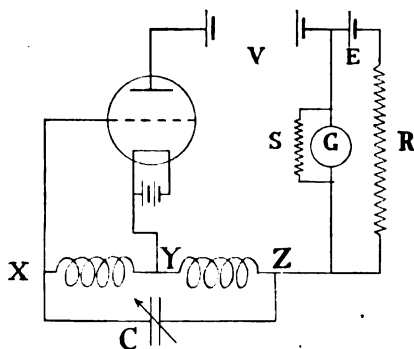
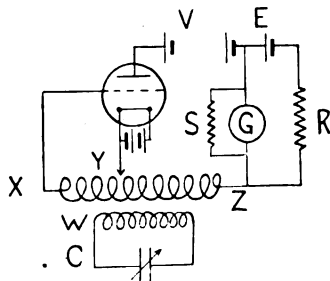


Fig. 4.



separate coil for the oscillation circuit. To complete the consideration of practical circuits, we will give some results obtained with circuits made up with the flat coils.

In order to display the extent of the range of constant sensitivity, a special “micrometer” condenser has been employed in some cases. This consists of the graduated fine adjustment movement of a Leitz microscope, to the table of which one of the condenser plates is fixed, while the other is carried at the end of a glass rod projecting from

the microscope tube. The micrometer screw is graduated to read  $1/200$  mm.

Fig. 5 shows the micrometer curves for a "tuned-grid" circuit, the coils of which were mounted parallel and about 1 cm. apart. The successive curves correspond to different degrees of coupling obtained by lateral displacement of the coils. It is clear that the desired linear form is possessed over very wide ranges at certain adjustments.

Fig. 5.

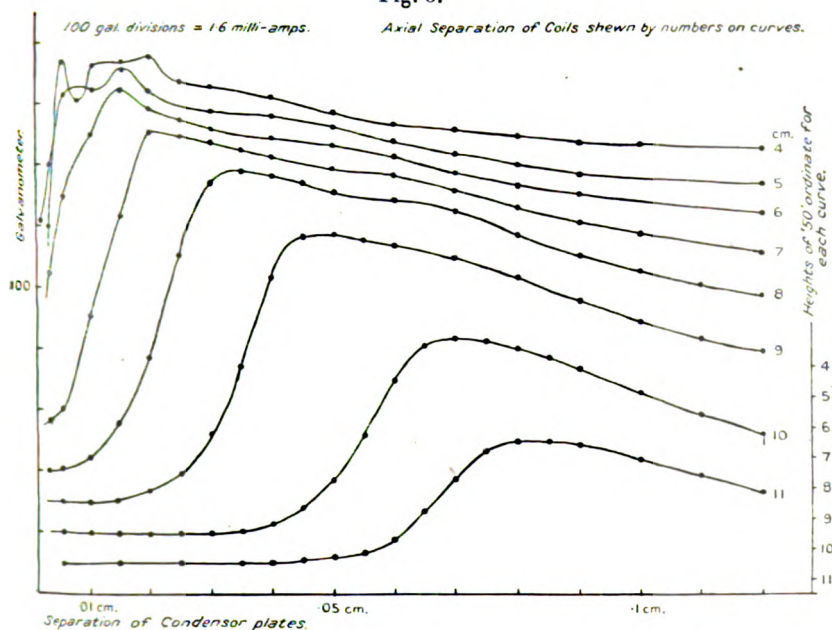
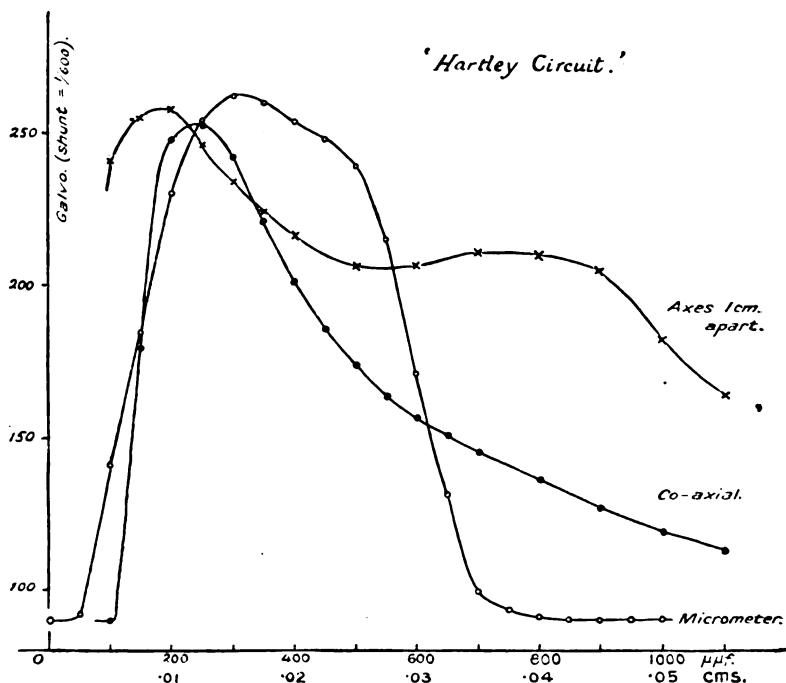


Fig. 6 shows three curves for a "Hartley" circuit constructed from the same pair of coils, mounted in series opposition (fig 3). We may note that the adjustment is quite critical, a displacement of 1 cm. from the co-axial position distorting the "capacity-current" curve completely. The "micrometer" curve is taken in the co-axial position, and shows an almost perfect linear form on either branch, great sensitivity being attainable. The adjustment is critical also in respect to closer approach of the coils. A Hartley circuit usually ceases to oscillate if we mount the coils too near together; in fact, the best "micrometer" adjustment is just on the border-line.

The functioning of these circuits is often found to be

improved by the introduction of a "blocking" condenser (say  $\cdot 05$  or  $\cdot 1 \mu f.$ ) between the anode and the point Z. A large condenser like this has two beneficial effects. In the first place, it minimises external "capacity" effects. The zero shunt, galvanometer, and H.T. battery are of necessity external to the rest of the apparatus, and the first-mentioned has occasionally to be handled by the observer. The presence of a large capacity in this part

Fig. 6.



of the apparatus tends to swamp transient capacity effects due to movements of the observer near by. In the second place, the secondary maxima and shoulders on the curves, if present, are considerably diminished or entirely eliminated in the presence of the blocking condenser. I have to thank Miss Katharine Preston, who investigated this latter point for me. She found that by starting with a small blocking condenser and gradually increasing it, one of the maxima moved, as it were, across the curve and ultimately disappeared with a sufficiently large capacity.

Miss Preston also investigated the effect of resistance in these oscillating circuits\*. As one would expect, this is very considerable. Although, in general, it may be stated that for high sensitivity (steep curves) the aim should be to keep the resistance in the oscillating coils low, nevertheless it is possible to overshoot the mark in this respect.

With coils of low resistance the effect of change of capacity is so great that instability sets in. A sort of hysteresis is displayed. The circuit refuses to start oscillating until the capacity is altered to a value well within the oscillating range; while, when oscillating, the circuit continues to do so for values of capacity for which it previously refused to respond. In each case oscillation starts or stops suddenly. A clue to this behaviour is forthcoming when we consider the probable theory of the micrometer circuits.

The usual methods of formulating the necessary conditions for oscillation maintenance in a circuit are, of necessity, only approximate. They do not yield a value for the change in the d.c. component of the anode current. This is, however, considerable, except in the case when the valve is oscillating about the mid-point of its characteristic. It is this anode-current effect that we employ in a micrometer circuit. In the absence of a satisfactory theory a general statement of the case is all that is possible.

If the "tuned circuit" has *little ohmic* resistance, it acts as if it possessed very *great* resistance at its natural frequency. Consequently the capacity adjustment must be carried far into the range of oscillation before this sets in. When oscillations have started, however, the effective resistance of the valve will drop. This, to some extent, compensates the reactance effect. The reverse capacity adjustment can then be carried out without stopping the oscillations. This, rather rough, version of the matter serves to explain the hysteresis effect. The result of inserting, say, 500 or 1000 ohms in series with the condenser is to *reduce* the "resonance" reactance effect. The oscillations now start and cease at almost the same value of the capacity, and no noticeable "hysteresis" is displayed. It is an attractive problem to consider whether the ideas here put forward have any bearing on wireless telegraphic practice; but this is beside our present interest.

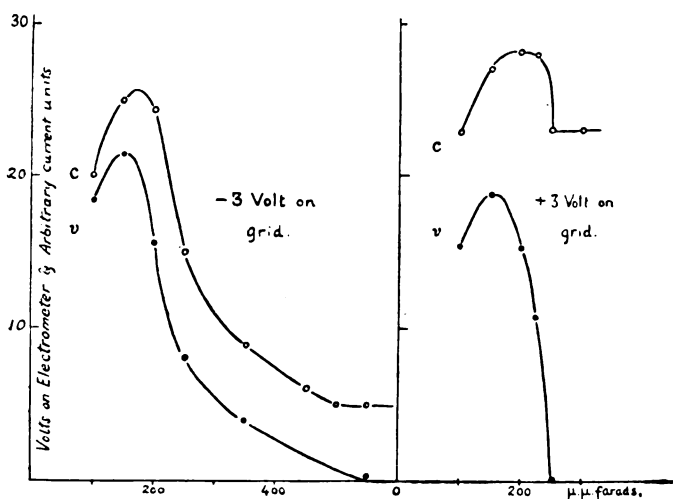
\* Dowling & Preston, *Phil. Mag.* vol. xliii. p. 537 (March 1922).



The other effect of resistance is to reduce the amplitude of the oscillation in the tuned circuit. This is accompanied by a corresponding reduction in the anode current.

The only other factor to be considered is the grid potential. In this connexion it will be observed that the circuits described have a direct metallic connexion between the grid and the negative terminal of the filament. With some valves a few volts—usually negative—have to be applied to the grid. I have not tried the grid-leak-condenser device for this purpose, as the necessary high resistance for the purpose would either be too bulky or else unsteady.

Fig. 7.



Some experiments were carried out for me by Mr. A. Fynn, S.J., to investigate experimentally how the amplitude of the oscillation in the tuned circuit depended on the grid potential; how it varied with the capacity in circuit; and, incidentally, the relation between it and the anode current. The usual ultramicro-meter circuit was set up, using a variable air condenser, and a sensitive Dolezalek electrometer, connected ideostatically, was used to determine the r.m.s. potential on the condenser. Fig. 7 shows the type of results so obtained. For moderate negative values of the grid potential (left-hand curve) we obtain considerable anode-current variation, and the amplitude of oscillation

risers and falls similarly with the capacity changes. There is a noticeable lag of the anode current behind the oscillation voltage. For the other curve, taken with a positive grid potential which corresponds to a point near the middle of the valve characteristic, the result is very different. Little anode-current variation occurs, while the strength of the oscillation is also somewhat less. This is quite what one would have expected. The second case is that which is best for the production of pure harmonic oscillations; the first is, of course, the best for micrometer applications. (This is also the more efficient adjustment of the valve as a generator of oscillations, although there are generally harmonics present.)

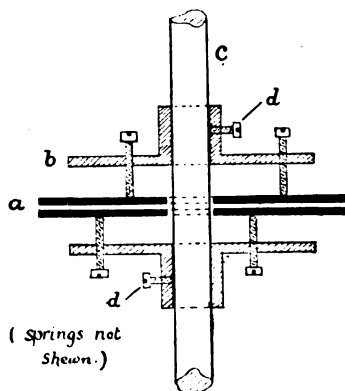
One point remains before we conclude with the general principles of these circuits. So far the coils and condensers considered have been such as to generate radio-frequency oscillations ( $10^5$  to  $10^7$  ~). I have, however, been able to obtain similar behaviour from circuits oscillating with frequencies as low as 500 ~. These require large capacities naturally and cannot be employed as micrometer devices, but capacity measurements at audio frequencies could be carried out with them.

We now proceed to give an account of some of the results obtained with these circuits and to discuss certain of their applications. It may be mentioned in this connexion that in most cases my aim has been to determine the best results obtainable under ordinary working conditions. None of my experiments have yet been carried out with the apparatus completely shielded. This could easily be done with the more recent forms of the apparatus, in which the galvanometer, micrometer circuit, and batteries altogether occupy about two cubic feet of space. However, my present experiments do not call for the highest sensitivities, and I dispense with this refinement. Even without such precautions the apparatus is extraordinarily steady, due no doubt to the damping and inertia of the galvanometer.

To measure moderate sensitivities the micrometer condenser already referred to is very convenient, but for very high sensitivities I use the condenser arrangement shown in fig. 8. The two plates (*a*) are supported on the ebonite collars (*b*) by suitable adjusting screws and springs. The ebonite collars are each clamped to the steel rod (*c*) by three set screws (*d*) which grasp the rod at points 5 cm. apart. The condenser plates are circular steel disks, 10 cm.

diameter, turned to a plane surface and bored 3 mm. larger than the steel rod, which is of 12 mm. diameter. The rod stands vertically and carries a small wooden platform above. To move the plates together, weights are placed on this platform which obviously causes the plates to approach by the amount of compression produced in the 5 cm. length of the rod by the added weight. Slight bending, due to

Fig. 8.



excentric location of the weight, will produce little error in view of the construction. The following table gives the results of one such determination :—

TABLE I.

Compression weight (kilogrammes).	Galvanometer scale reading.	Deflexion for 500 grammes.
0.0	- 187	—
0.5	- 105	82
1.0	- 27	78
1.5	+ 45	72
2.0	+ 121	76

The differences between the numbers in the last column are partly due to too tight a fit of the ebonite collars of the condenser on the rod, and partly to want of screening of the apparatus. The observations indicate an average deflexion of 154 divisions per kilogramme. The calculated compression corresponding to this is  $2.16 \times 10^{-6}$  cm. One galvanometer division should correspond to  $1.4 \times 10^{-8}$  cm.

This would probably have been the sensitivity under "screened" conditions, but the actual observations cannot be regarded as showing this sensitivity. The maximum variation of the numbers in the last column of Table I. from their mean is 5. Thus there would be an uncertainty in any reading of  $5 \times 1.4 \times 10^{-8}$  ( $= 7 \times 10^{-8}$ ) cm.: that is, a sensitivity of  $10^{-7}$  cm. per galvanometer scale-division can be reckoned on.

The application of the recording ultramicrometer to the determination of minute displacements, changes of length, and the like, does not call for a detailed description. In view of the wide range of constant sensitivity, no very delicate adjustments need be provided for the condenser plates. In most cases, I mount one on a micrometer screw for calibration purposes, and the other with three adjustment screws like those shown in fig. 8. For very fine measurements the micrometer screw is made to work against a weak spring, which is attached to the much more rigid cantilever plate-support; this well-known device enables a minute plate movement to be effected, but requires preliminary calibration in some other way. The members supporting the plates are of course attached suitably to the two systems whose relative movement is to be recorded.

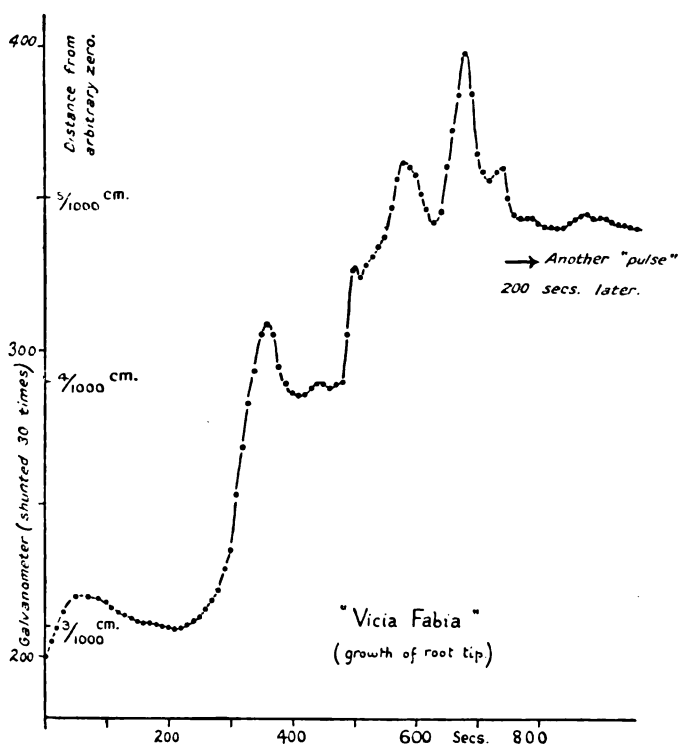
An important application of the device is in the construction of an extensimeter. Ewing, writing in the 'Encyclopædia Britannica,' states that, using the customary 8-inch specimen, "it is desirable to read the extension to, say,  $1/50,000$  inch, if the modulus of elasticity is to be found with fair accuracy, or if the limits of proportionality of stress and strain are under examination." In other words, it is desirable to measure to within two-millionths of a centimetre per centimetre length. Our apparatus could easily record this latter amount, and *it would not be necessary to use a specimen even one inch long*. Furthermore, by attaching condenser plates so as to record the *lateral* strain, the determination of Poisson's ratio (and therefore all the elastic constants) would be possible with quite small specimens.

It may be objected that there is little space available around the specimen in a testing machine. In applying the method the condenser plates, themselves quite small, are the only parts that have to be near the specimen. The oscillation circuit proper is situated several feet away, and connected to the condenser by a pair of wires about an inch apart (*separated, not twisted*). I have tried out a device of this kind and found it answered satisfactorily. There may

be slight "capacity" effects if the operator approaches too near the condenser wires, but it is easy to arrange the apparatus so that these can be screened.

A very important consideration, in a recording device is whether it responds to rapid variations of the observed phenomenon. With the usual ultramicrometer circuits the only limit in this connexion arises in the galvanometer. An excellent example of the utility of the ultramicrometer for following minute irregular movement arises in the study of plant growth\*. Using a galvanometer, rated

Fig. 9.



as having a period of 2.5 secs. but almost dead-beat, it was apparently possible to follow movements whose duration was about 10 seconds. Fig. 9 shows a series of observations of the galvanometer when the root-tip of *Vicia Fabia* was under examination. The lower condenser plate

\* Dowling, 'Nature,' June 23rd, 1921.

was mounted on a micrometer screw; the upper, almost parallel to it, was carried on the end of a light flat spring. The root-tip, growing of course downwards, pressed against a light wooden arm projecting from the upper plate. It was found that the maximum deflexion of the spring due to the whole extent of growth observed could be produced by a force of a few milligrammes, and thus the pressure on the plant only amounted to a few dynes. The growth pulses noticed by Bose\* are shown very convincingly. Check experiments under closely similar conditions (with *dead* plants) show absolutely no recorded motion. Unfortunately, the two students of botany who kindly assisted me in this plant-growth work—Miss Cannon and Mr. Saunders—are no longer available, and this work has had to be postponed.

One of the earliest applications I made of the device was to record the minute flexure of the diaphragm of a pressure gauge. The (india-rubber) diaphragm carried one of the condenser plates; the other was mounted on a bridge across the air chamber, the usual adjustment screws being provided. My aim was to obtain a very robust pressure gauge, and I employed stout sheet rubber (1 mm. thick) stretched tightly across the air chamber (10 cm. diameter). To facilitate adjustments a small variable condenser was connected in *parallel* with the pressure-gauge condenser. I found that *both* sides of the gauge had to be enclosed in view of the high sensitivity. With one of these (*thick rubber*) I found the readings quite steady; the zero-keeping qualities and rapidity of action very high; while consistent readings could be obtained to less than  $\frac{1}{3}$  of one-millionth of an atmosphere ( $0.32$  dyne per  $\text{cm.}^2$ , to be exact). In this particular case the galvanometer was still shunted 10-fold, which was necessary for two reasons: (1) as usual, no screening was employed; (2) the pressures being measured were due to the pressure drop accompanying the slow flow of air through a 1-cm. diameter (50 cm. long) brass tube, and it was impossible to avoid slight irregularities in the air stream.

For the information of those interested in gas-flow measurement, I may here mention that the slowest velocity actually dealt with was 14 cm. per sec., which produced 31 mm. deflexion on the galvanometer, while the latter was consistent to 1 mm. with the 10 shunt used. With a Pitot tube (for which pressure varies as square of air

\* Bose, Phil. Trans. Roy. Soc. B. vol. xc. p. 364, Feb. 1919.

velocity) I found that an air stream of about 80 cm. per second could be measured with about the same accuracy. These numbers are *conservative statements* of results obtained *under ordinary laboratory conditions*.

I have not hitherto tried the micrometer for indicating the changes in level of liquids, but there does not appear to be any reason why it should not be so employed. In this way, using mercury, it should be possible to record  $10^{-7}$  cm. (pressure difference) without difficulty, or, with other liquids, perhaps lower differences still. Special difficulties are presented by the problem of high vacuum pressures, but the manifest advantages of a direct-reading gauge for these encourages one to persevere in this direction.

Interesting possibilities arise if we consider the incorporation of the ultramicrometer as the recording device in a spring balance. In other brief publications, I have indicated how it can be employed to dispense with the small weights and riders of a sensitive balance. Rapidity of action and very high sensitivity are in this case no longer incompatible. However, except for special work, I imagine that most users of balances would look askance on the necessary batteries, galvanometer, and other apparatus. I have constructed an instrument, however, by which it is possible to weigh 200 grammes to the nearest  $1/10$  milligramme in about a quarter of a minute.

The principle employed in these balances has other interesting applications, and it will be worth while explaining it more fully. Suppose Hooke's law to be obeyed. Then  $Se = Mg$ , where  $e$  = total extension due to mass  $M$  and  $S$  is a constant. Small changes in  $e$  are indicated by attaching one of our condenser plates to the extremity of the spring. In a balance the load is kept within a fraction of a gramme (say) of a standard load  $M$  by removing weights when placing the body in position. The galvanometer indicates by how many milligrammes (say) the total load differs from  $M$ .

The same device should also indicate changes in  $g$ . Here there are three cases to be considered: (1) variation of terrestrial gravity from place to place; (2) variation of the vertical gravitational force due to the tide-generating forces of sun and moon; (3) "Newtonian attraction" experiments due to the introduction of a heavy mass beneath. The last-mentioned type of problem is, comparatively, a simple proposition. With a view to testing its possibility, I set up an apparatus in which a weight of about 1 kilo was suspended by a long silk cord from a

steel spring. The spring extension was about 25 cm. and the condenser plate was attached to the spring, the silk cord passing down through a hole pierced in the lower (fixed) condenser plate. The silk cord enabled the electrical circuit to be shielded from the possible capacity effects accompanying the movements of the large attracting mass of about 50 kilos of lead. The sensitivity required was very high, a simple calculation showing that, if the attracting masses were about 25 cm. apart, the extension to be expected is only  $1/8,000,000$  cm. By working late at night and remaining almost motionless during the observations, I was able to secure a sensitiveness such that the galvanometer showed a deflexion of about 300 scale-divisions each time the heavy mass was wheeled into place. My purpose in making this experiment was, principally, to ascertain whether the electrostatic attraction between the condenser plates would cause instability in the system. No sign of this effect was perceived.

The two other gravitational effects are much larger than that dealt with in the experiment, but involve special difficulties. These arise in both cases from the fact that the micrometer would be called on to measure the displacement occurring at long intervals of time. I have not yet been able to carry out satisfactorily experiments to test the possibility of determinations of this kind.

The ultramicrometer lends itself specially well as a recorder for a seismometer. Thanks to the kindness of the Rev. W. O'Leary, S.J., who constructed a new type of vertical seismometer for me, I was enabled to carry out some trials in this connexion. I am now, however, conducting further experiments on this matter, and shall reserve a full account of all the work for a later communication.

Perhaps the most important application of the ultramicrometer is one on which I am still engaged. A full account will, I hope, be ready for publication shortly. Thanks to the great rapidity with which the oscillatory circuit responds to the movements of the condenser plate, it is possible to use the apparatus to measure the rapidly varying stresses in machinery. Thus the out-of-balance forces on the bearings of a rotor can be determined by a suitable adaptation of the method, and the necessary data obtained for correcting the out-of-balance condition. In this connexion the use of a high-frequency oscillograph might be employed, but there are serious objections to this. Such instruments are very insensitive, and necessitate the



use of power valves operating at perhaps 1000 volts. I was enabled to carry out some experiments with ultramicrometer circuits, employing such high-power valves with a Duddell oscillograph, thanks to the courtesy of the Cambridge-Paul Company, who lent me the latter instrument. Apart from its comparative insensitiveness, the apparatus was otherwise satisfactory, but both dangerous and troublesome to separate. For these reasons, I have abandoned this method of attack for one in which an ordinary slow-period, sensitive galvanometer is employed in conjunction with a synchronous contact device. This arrangement has now been in use for some months and has fulfilled every requirement.

In this paper I have confined myself to an account of those applications of the ultramicrometer actually realized, and have avoided quoting any observations with the apparatus in such a super-sensitive condition as to render shielding and other precautions necessary. I hope, in due course, to take up this aspect of the problem, and to determine the highest working sensitivity obtainable under specially favourable conditions. One of the most serious difficulties which has to be dealt with when working at very high sensitivity is the tendency of the galvanometer to "creep." Great care is necessary in selecting the cells (accumulator and high-tension batteries) to ensure that they are in good condition. It is *absolutely necessary* to use for the zero shunt cells of identical construction to those in the H.T. anode battery. Temperature fluctuations, however small, must be avoided. Even barometric and humidity variations may conceivably affect the coils or condenser. It must be remembered how small a variation in the circuit constants will affect the anode current to a measurable extent, and seemingly unimportant factors should be carefully considered. Finally, for the higher sensitivity, one must guard against effects due to the creeping of an electrostatic charge on the interior of the valve bulb. If this cannot be prevented, at least one must wait long enough for a steady condition to be attained. The only general rule that can be given is to make the apparatus function as near the foot of the "capacity-current" curve as possible; by so doing, the minimum demand is made on the batteries, and they are less likely to change. Similarly, it is better to seek sensitivity by using a good galvanometer than by running the filament at a higher temperature. I generally use only 4 volts.

VII. *A Note on the Fluctuation of Water-Level in a Tidal-Power Reservoir.* By Prof. S. CHAPMAN, M.A., D.Sc., F.R.S., University of Manchester \*.

§1. **T**HIS note relates to the variation of water-level in a tidal basin separated from the sea or from an estuary by a dam, in which there are sluices constantly submerged, through which water may freely flow in and out. Corresponding to a known periodic variation of level in the sea there will result a periodic rise and fall of level in the basin, and it is sought to determine the amount and character of this fluctuation. The problem is of some practical interest, since a periodic difference of height between such a basin and the sea may be used for the development of water-power, during the periods both of inward and outward flow. The insertion of turbines in the sluices modifies the rate of flow of water, but the consideration of the results for the open sluices is the first step towards ascertaining the available power.

The most important case is that in which  $H$ , the height of water in the sea, does not differ much from a simple sine-function of the time, with a period equal to half a lunar day, or 12 hours 25 minutes. Thus, let

$$H = H_0 \sin \alpha t, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where  $H_0$  is half the tidal range,  $t$  is time reckoned in seconds from the epoch of mean level during the rise of tide, and

$$\alpha = 2\pi / 12\frac{25}{30} \times 60 \times 60 \quad . \quad . \quad . \quad . \quad (2)$$

The height of water in the basin will be denoted by  $H'$ , while the difference of height (the working head) will be denoted by  $h$ , i. e.

$$h = H - H'. \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The velocity of flow,  $v$ , through the sluices will be calculated by the usual approximate formula

$$v^2 = 2g |h|, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where  $|h|$  denotes the numerical (positive) value of  $h$ , and  $g = 32.2$ .

Let  $a$ ,  $A$  denote respectively the sectional area of the combined sluices and of the basin,  $A$  being assumed the same

\* Communicated by the Author.

for all depths  $H'$ . Then the differential equation connecting  $H$  and  $H'$  or  $h$  is

$$\frac{d(AH')}{dt} = av = \pm a(2g|h|)^{1/2} \quad . \quad . \quad . \quad (5)$$

or

$$\frac{dA(H-h)}{dt} = \pm a(2g|h|)^{1/2}, \quad . \quad . \quad . \quad (6)$$

where the sign of the last term is that of  $h$ .

An exact general solution of this equation, when  $H$  is an arbitrary periodic function of the time, must be difficult to obtain, on account of the transference of the sign of  $h$ , on the right-hand side, to the outside of the radical  $(2g|h|)^{1/2}$ . The problem was proposed to the writer some years ago, without result, by Prof. A. H. Gibson, who thereafter solved it in a number of special cases by a convenient graphical method based partly on successive trial. In these cases, which seem to lie within the range of values of most importance in practice,  $H$  was either a pure sine function, or nearly so (the latter case related to spring tides, in which the rise of level took place rather more quickly than the fall); the fluctuation within the basin proved to be a close approximation to a sine curve, the higher harmonic components in  $H'$  being very small. This result suggested to the writer the following treatment of the problem, which leads to a convenient expression for the leading component in  $H'$  or  $h$ , agreeing within two or three per cent. with the results found by Prof. Gibson, and obviating the special graphical solution of each particular case.

§ 2. It is assumed that  $H'$  or  $h$  can be represented approximately by a simple sine curve, viz.,

$$h = h_0 \sin(\alpha t + \epsilon), \quad . \quad . \quad . \quad (7)$$

where  $h_0$  is positive. In this case it is not difficult to represent  $\pm |h|^{1/2}$ , where the sign is that of  $h$  itself, by a Fourier's series. In so doing, it is convenient, for the moment, to neglect the phase-constant  $\epsilon$ , and to write

$$\pm \sin \alpha t^{1/2} = a_1 \sin \alpha t + a_3 \sin 3\alpha t + a_5 \sin 5\alpha t + \dots, \quad (8)$$

since it is evident that only sine terms involving odd multiples of  $\alpha t$  will appear in the series. The coefficient

$a_n$  is given by

$$a_n = \frac{4\alpha}{\pi} \int_0^{\pi/2} (\sin \alpha t)^{1/2} \sin n\alpha t dt = \frac{4}{\pi} \int_0^{1/2\pi} (\sin x)^{1/2} \sin nx dx, \quad (9)$$

which may be evaluated in general terms by the expansion of  $\sin nx$  in a series of products of sines and cosines of  $x$ . It is sufficient, however, to determine the first two or three terms: thus, writing  $\sin x = u^{1/2}$ ,

$$a_1 = \frac{4}{\pi} - \frac{1}{2} \int_0^1 u^{1/4} (1-u)^{-1/2} du = \frac{2}{\pi} B\left(\frac{5}{4}, \frac{1}{2}\right) = \frac{2}{\pi} \frac{\Gamma(\frac{5}{4})\Gamma(\frac{1}{2})}{\Gamma(\frac{7}{4})}, \quad (10)$$

where

$$\Gamma(\frac{1}{2}) = \pi^{1/2}, \quad \Gamma(\frac{5}{4}) = 0.9063, \quad \Gamma(\frac{7}{4}) = 0.9189, \quad (11)$$

so that

$$a_1 = \frac{1}{\pi^{1/2}} \frac{0.9063}{0.9189} = 1.113. \quad (12)$$

Similarly,

$$a_3 = \frac{2}{\pi} \int_0^1 (3u^{1/4} - 4u^{5/4})(1-u)^{-1/2} du = 3a_1 - 4 \cdot \frac{5}{7} a_1 = \frac{1}{7} a_1, \quad (13)$$

$$a_5 = a_1 \left( 5 - 20 \cdot \frac{5}{7} + 16 \cdot \frac{9 \cdot 5}{11 \cdot 7} \right) = \frac{5}{77} a_1, \quad (14)$$

and so on. Consequently

$$\pm \sin \alpha t^{1/2} = 1.113 (\sin \alpha t + \frac{1}{7} \sin 3\alpha t + \frac{5}{77} \sin 5\alpha t + \dots), \quad (15)$$

while

$$\begin{aligned} \pm (2gh)^{1/2} &= \pm (2gh_0 \sin(\alpha t + \epsilon))^{1/2} \\ &= 1.113 (2gh_0)^{1/2} \left\{ \sin(\alpha t + \epsilon) + \frac{1}{7} \sin 3(\alpha t + \epsilon) + \dots \right\}, \end{aligned} \quad (16)$$

Hence, if  $H$  is of the form (1), the equation (6) may be written

$$\alpha A \{ H_0 \cos \alpha t - h_0 \cos(\alpha t + \epsilon) \} = 1.113 (2gh_0)^{1/2} \left\{ \sin(\alpha t + \epsilon) + \frac{1}{7} \sin 3(\alpha t + \epsilon) + \dots \right\}, \quad (17)$$

or, writing

$$t' = \alpha t + \epsilon, \quad (18)$$

(6) becomes

$$H_0 \cos(t' - \epsilon) - h_0 \cos t' = (2kh_0)^{1/2} (\sin t' + \frac{1}{7} \sin 3t' + \dots), \quad (19)$$

where

$$(2k)^{1/2} = 1.113 \frac{(2g)^{1/2} \alpha}{A},$$

or, if  $\alpha$  is given by (2),

$$k = 2.018 \cdot 10^3 (\alpha/A)^2. \quad (20)$$

The equation (19) can be satisfied by suitable choice of  $h_0$  and  $\epsilon$ , provided the terms representing the third and higher components of  $\pm |h|^{1/2}$ , on the right, are negligible. Whether this is the case, or not, is a matter for subsequent examination (§5); assuming it to be so, (19) is satisfied if

$$h_0 = H_0 \cos \epsilon, \quad H_0 \sin \epsilon = (2kh_0)^{1/2}. \quad (21)$$

Hence, by squaring and adding,

$$H_0^2 = h_0^2 + 2kh_0, \quad (22)$$

so that, remembering that  $h_0$  is positive,

$$h_0 = (H_0^2 + h^2)^{1/2} - k. \quad (23)$$

After thus determining  $h_0$ , the phase angle  $\epsilon$  is given by

$$\tan \epsilon = (2k/h_0)^{1/2}. \quad (24)$$

The equations (23, 24) determine the approximate value of the "working head"  $h$ , i.e., the difference of level on the two sides of the dam. The height  $H'$  inside the basin is then given by

$$\left. \begin{aligned} H' &= H - h = H_0 \sin \alpha t - h_0 \sin (\alpha t + \epsilon) \\ &= (H_0 - h_0 \cos \epsilon) \sin \alpha t - h_0 \sin \epsilon \cos \alpha t \\ &= H_0' \sin (\alpha t - \theta) \end{aligned} \right\}, \quad (25)$$

where

$$H_0' \cos \theta = H_0 - h_0 \cos \epsilon, \quad H_0' \sin \theta = h_0 \sin \epsilon. \quad (26)$$

Thus

$$\left. \begin{aligned} H_0'^2 &= H_0^2 + h_0^2 - 2H_0h_0 \cos \epsilon \\ &= H_0^2 - h_0^2 = 2kh_0 \end{aligned} \right\}, \quad (27)$$

by (21), (22), while

$$\tan \theta = \frac{h_0 \sin \epsilon}{H_0 - h_0 \cos \epsilon} = \frac{h_0 \sin \epsilon \cos \epsilon}{H_0 \cos \epsilon - h_0 \cos^2 \epsilon} = \frac{\sin \epsilon \cos \epsilon}{1 - \cos^2 \epsilon} = \cot \epsilon, \quad (28)$$

so that

$$\theta = \frac{\pi}{2} - \epsilon, \quad (29)$$

and

$$H' = (2kh_0)^{1/2} \cos (\alpha t + \epsilon). \quad (30)$$

These results also follow easily from a vector diagram; if vectors are drawn to represent  $H_0$  and  $h_0$ , the latter being in advance of  $H_0$  by an angle  $\epsilon$ , the equation  $h_0 = H_0 \cos \epsilon$  indicates that the vector  $H_0 - h_0$ , joining the ends of the vectors  $H_0$  and  $h_0$ , is perpendicular to  $h_0$  (i.e., it has a lag

equal to  $\frac{1}{2}\pi - \epsilon$ ), and that its magnitude is  $H_0 \sin \epsilon$  or  $(2kh_0)^{1/2}$ .

§3. These results may be compared with those obtained graphically by Prof. Gibson for certain special cases\*. The first series of these refer to the case when

$$H = 8 \sin nt, \quad . \quad . \quad . \quad . \quad . \quad (31)$$

where  $n$  differs slightly from  $\alpha$ , as given in §2 (2), because the period assumed was 13 hours; the corresponding value of  $k$  is  $2.214 \cdot 10^3 (a/A)^2$ . The values of  $A/a$  considered by Prof. Gibson were 16000, 20000, 25000, and 30000. His curves for  $H'$  have been harmonically analysed, and the values of  $H_0'$  and  $\theta$  for the leading component thus found; from them the semi-amplitude  $h_0$  and phase  $\epsilon$  of the leading component of  $h$  ( $=H-H'$ ) have been calculated; they are given below, together with the values of  $k$ ,  $h_0$ , and  $\epsilon$  determined by the formulæ of §2. The relations of §2 between  $H_0$ ,  $H_0'$ ,  $h_0$ ,  $\epsilon$ , and  $\theta$  are not exactly fulfilled by the graphically determined values, but the agreement between the following two sets of values of  $h_0$  (the most important quantity in practice) is satisfactory.

$A/a$ .....	16000	20000	25000	30000
$k$ .....	8.65	5.53	3.54	2.46
$h_0$ (calc.) ..	3.14	4.19	5.21	5.91
$h_0$ (graph.) ..	3.17	4.30	5.21	5.84
$\epsilon$ (calc.) ....	67°	58°	49°	42°
$\epsilon$ (graph.) ..	62	55	47	41

In the second series of curves given by Prof. Gibson, the period was taken as  $12\frac{1}{2}$  hours, and  $H$  was no longer represented by a pure sine curve; the curve represented the spring tides at Portishead in the Severn Estuary, and on harmonic analysis (taking the phase of the first component as zero) the following were found to be the leading terms in its Fourier's series:

$$21.0 \sin at + 2.4 \sin 2at + 0.66 \sin 3at. \quad . \quad . \quad . \quad (32)$$

Two values of  $A/a$  were considered, viz., 12,000 and 16,000. Proceeding as before, the following results were obtained by

\* 'Engineering,' Dec. 17, 1920, p. 794.

analysis of Prof. Gibson's graphs of  $H'$ , and by calculation from the formulæ of § 2.

$A/a$ .....	12000	16000
$h$ .....	14.21	7.99
$h_0$ (calc.) ..	11.1	14.5
$h_0$ (graph.) ..	11.4	15.2
$\epsilon$ (calc.) ....	58°	46°
$\epsilon$ (graph.) ..	53	43

The differences between the two sets of values of  $h_0$  are here slightly greater than before, though still less than 5 per cent.

*Sluice area for maximum power.*

§ 4. The power obtainable by using the inward and outward flow of water through the sluices is proportional (i.) to the sluice area  $a$ , and (ii.) to the mean square velocity of the water, *i. e.* to the mean value of  $|h|$ . When  $h$  is a pure sine-function, or nearly so, the semi-amplitude being  $h_0$ , the power available is therefore proportional to  $ah_0$ , and it is of interest to determine what ratio of sluice-area to basin-area, for a given basin-area  $A$  and tidal range  $2H_0$ , gives the maximum power. Since  $a/A$  occurs only in  $h$ , which is proportional to  $(a/A)^2$ , the condition for maximum power is clearly

$$\frac{dk^{1/2}h_0}{dk} = 0,$$

or

$$\frac{dk^{1/2}\{(k^2 + H_0^2)^{1/2} - k\}}{dk} = 0,$$

or

$$\frac{1}{2k^{1/2}}\{(k^2 + H_0^2)^{1/2} - k\} + k^{1/2}\left\{\frac{k}{(k^2 + H_0^2)^{1/2}} - 1\right\} = 0,$$

which reduces to

$$k = \frac{1}{3}H_0, \quad \dots \dots \dots (33)$$

or

$$\frac{a}{A} = \frac{\alpha H_0^{1/2}}{1.113(3\eta)^{1/2}} \dots \dots \dots (34)$$

The most economical ratio of sluice-area to basin-area is thus proportional to the square root of the tidal range.

With the value of  $\alpha$  corresponding to a lunar semi-diurnal tide (*cf.* (2)) the above result is equivalent to

$$\frac{A}{a} = 7.79 \cdot 10^4 H_0^{-1/2},$$

so that if  $H_0 = 21$  ft.,  $A/a = 17,000$ . In the case of the first set of Prof. Gibson's curves, where the period of the tide was taken as 13 hours, the corresponding value of  $A/a$  would be  $8.15 \cdot 10^4 H_0^{-1/2}$ , so that if  $H_0 = 8$ , the best value of  $A/a$  is 28,800. By inference from his graphical results, Prof. Gibson estimated these two ratios of  $A/a$  as 16,000 and 30,000 respectively.

§5. It remains to consider how far the neglect of the higher harmonic terms in  $h$  is likely to affect the estimate of the available power. The coefficients of the neglected third and fifth harmonics in  $|h|^{1/2}$  in (19) are  $1/7$  and  $5/77$  times the coefficient of the leading term in  $|h|^{1/2}$ , and it would seem as if the odd harmonics in the true value of  $h$  bear smaller ratios than these to the leading term, while the even harmonics are small, if not zero. The coefficients of the second harmonics in  $H'$  or  $h'$  corresponding to the four values of  $A/a$  in Prof. Gibson's first set of curves are 0.03, 0.04, 0.00, 0.06, while the corresponding coefficients of the third harmonics are 0.39, 0.28, 0.57, 0.47; part of these may be due to slight errors in measuring the curves. Now the utmost extent to which the mean value of  $|h|$  can be affected by a harmonic of frequency  $n$  and amplitude  $a_n$  is easily seen to be  $a_n/n$ . In the cases cited this is quite negligible. Even for the spring-tide curves discussed in §3, where  $H$  was itself not a pure sine-function (*cf.* §2) the second and third harmonic terms in  $h$ , as derived graphically, were only 1.47 and 0.70 ( $A/a = 12,000$ ) and 0.70, 0.63 ( $A/a = 16,000$ ). The second harmonics would in these cases affect the mean value of  $|h|$  very little, because the periods of inflow and outflow for the reservoir are very nearly equal. Thus, though the analysis of this paper could be extended, if necessary, so as to afford an approximation to at least the next most important harmonic component in  $h$  after the first, there appears to be no practical necessity for so doing.

### Summary.

§6. The difference of height,  $h$ , between (i.) a sea or estuary undergoing a tidal change of water-level, in half a lunar day, represented by  $H_0 \sin at$ , and (ii.) a tidal basin of area  $A$  connected with the sea by sluices of area  $a$ , is represented by the approximate formula

$$h = h_0 \sin (at + \epsilon),$$



where  $h_0$  and  $\epsilon$  are given by

$$h = (H_0^2 + k^2)^{1/2} - k, \quad \tan \epsilon = (2k/h_0)^{1/2}$$

in terms of the number  $k$ , where

$$k = 2.018 \cdot 10^9 (a/A)^2.$$

The ratio of  $A$  to  $a$  which corresponds to the maximum power-development from this difference of head is given by

$$A/a = 7.79 \cdot 10^4 H_0^{-1/2},$$

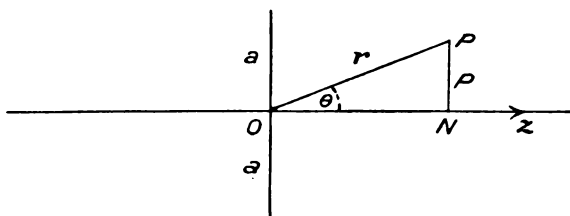
where  $H_0$  is supposed measured in feet.

VIII. *Note on the Magnetic Field produced by Circular Currents.* By T. J. I' a. BROMWICH, Sc.D., F.R.S., Fellow and Professor in Mathematical Science, St. John's College, Cambridge\*.

PROF. H. NAGAOKA has investigated these magnetic fields by means of  $q$ -series in a recent number of this journal†; but it does not seem to have been noticed that his results can be found in a very elementary way by using Legendre's theorem that the potential of a symmetrical system can be determined when the form of the potential is known along the axis of symmetry.

1. *The field of a single circle (of radius  $a$ ).—At points on*

Fig. 1.



the axis of  $z$  the magnetic force due to unit current in the circular wire is equal to

$$\gamma = \frac{2\pi a^2}{(a^2 + z^2)^{3/2}} = \frac{2\pi}{a} \left( 1 - \frac{3}{2} \frac{z^2}{a^2} + \frac{3 \cdot 5}{2 \cdot 4} \frac{z^4}{a^4} - \dots \right),$$

provided that  $z$  is numerically less than  $a$ .

\* Communicated by the Author.

† Phil. Mag. vol. xli. p. 377 (1921).

Now the component of magnetic force in any fixed direction satisfies Laplace's equation; and in particular this is true of  $\gamma$ , the component parallel to the axis of symmetry.

Thus at points not on the axis the magnetic force  $\gamma$  is given by the series

$$\gamma = \frac{2\pi}{a} \left\{ 1 - \frac{3}{2} \frac{r^2}{a^2} P_2(\cos \theta) + \frac{15}{8} \frac{r^4}{a^4} P_4(\cos \theta) - \dots \right\} \\ = \frac{2\pi}{a} \left\{ 1 - \frac{3}{2a^2} \left( z^2 - \frac{1}{2} \rho^2 \right) + \frac{15}{8a^4} \left( z^4 - 3z^2 \rho^2 + \frac{3}{8} \rho^4 \right) - \dots \right\}. \quad (1)$$

The formula (1) agrees with Prof. Nagaoka's (18), (19); to obtain (20) we must include the following term in the bracket, which is

$$- \frac{35r^6}{16a^6} P_6(\cos \theta) = - \frac{35}{16a^6} \left( z^6 - \frac{15}{2} z^4 \rho^2 + \frac{45}{8} z^2 \rho^4 - \frac{5}{16} \rho^6 \right). \quad (2)$$

It will be observed that the coefficient of  $\rho^6$  is apparently erroneous in Prof. Nagaoka's formula.

The value of the magnetic potential  $V$  can now be found by integrating the equation

$$-\frac{\partial V}{\partial z} = \gamma.$$

This gives, at points on the axis,

$$V_0 - V = 2\pi \left( \frac{z}{a} - \frac{1}{2} \frac{z^3}{a^3} + \frac{1 \cdot 3}{2 \cdot 4} \frac{z^5}{a^5} - \frac{1 \cdot 3 \cdot 5}{2 \cdot 4 \cdot 6} \frac{z^7}{a^7} + \dots \right),$$

where  $V_0$  is a constant; and so, at any point, we have the formula

$$V_0 - V = 2\pi \left( \frac{r}{a} P_1 - \frac{1}{2} \frac{r^3}{a^3} P_3 + \frac{3}{8} \frac{r^5}{a^5} P_5 - \frac{5}{16} \frac{r^7}{a^7} P_7 + \dots \right).$$

When the last formula is written out in full we obtain the result

$$V_0 - V = 2\pi \left\{ \frac{z}{a} - \frac{1}{2a^3} \left( z^3 - \frac{3}{2} z \rho^2 \right) + \frac{3}{8a^5} \left( z^5 - 5z^3 \rho^2 + \frac{15}{8} z \rho^4 \right) \right. \\ \left. - \frac{5}{16a^7} \left( z^7 - \frac{21}{2} z^5 \rho^2 + \frac{105}{8} z^3 \rho^4 - \frac{35}{16} z \rho^6 \right) \right\}. \quad (3)$$

Thus on differentiation with respect to  $\rho$  we find  $\lambda$  the transverse component of the magnetic field

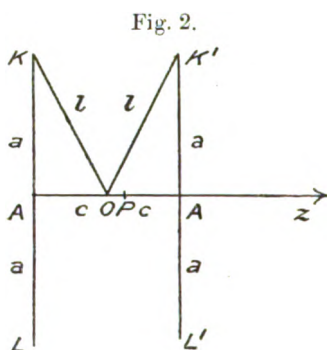
$$\lambda = \sqrt{(\alpha^2 + \beta^2)} = - \frac{\partial V}{\partial \rho} = \frac{2\pi z \rho}{a^3} \left\{ \frac{3}{2} + \frac{15}{16a^2} (3\rho^2 - 4z^2) \right. \\ \left. + \frac{105}{128a^4} (8z^4 - 20z^2 \rho^2 + 5\rho^4) + \dots \right\}. \quad (4)$$

The formula (4) agrees precisely with (15), (16), and (17) of Prof. Nagaoka's.

2. *Field near the centre of Helmholtz's galvanometer (double coils).*

Let the section be represented by the adjoining diagram (fig. 2) in which

$$a = 2c, \text{ and } l^2 = a^2 + c^2 = 5c^2.$$



$$2c = a, \quad l^2 = a^2 + c^2 = 5c^2$$

Since the field is symmetrical about the line of centres AA' (which we take as Oz), it will suffice to calculate the field at a point P on the axis (and near to O).

The magnetic force at the point P due to unit current in the coil A is known to be

$$\gamma_1 = \frac{2\pi a^2}{KP^3} = \frac{2\pi a^2}{\{a^2 + (c+z)^2\}^{3/2}}.$$

Now we have

$$a^2 + (c+z)^2 = l^2 + 2cz + z^2 = \left(l + \frac{cz}{l}\right)^2 + \left(\frac{az}{l}\right)^2.$$

Thus, since  $az/l^2$  is small, we can write

$$\begin{aligned} \gamma_1 &= \frac{2\pi a^2}{\{a^2 + (c+z)^2\}^{3/2}} = \frac{2\pi a^2 l^3}{(l^2 + cz)^3} \left\{ 1 + \left( \frac{az}{l^2 + cz} \right)^2 \right\}^{-3/2} \\ &= \frac{2\pi a^2}{(l^2 + cz)^3} \left\{ 1 - \frac{3}{2} \frac{a^2 z^2}{(l^2 + cz)^2} + \frac{15}{8} \frac{a^4 z^4}{(l^2 + cz)^4} + \dots \right\}. \end{aligned}$$

To obtain the same degree of accuracy as would be given

by Prof. Nagaoka's formulæ, we must expand as far as terms in  $z^4$ . Then the result is

$$\gamma_1 = \frac{2\pi a^2}{l^3} \left( 1 - \frac{3cz}{l^2} + \frac{6c^2 z^2}{l^4} - \frac{10c^3 z^3}{l^6} + \frac{15c^4 z^4}{l^8} \right) - \frac{3\pi a^4 z^2}{l^7} \left( 1 - \frac{5cz}{l^2} + \frac{15c^2 z^2}{l^4} \right) + \frac{15\pi a^6 z^4}{4l^{11}} \quad (5)$$

The magnetic force  $\gamma_2$ , due to the same current in the second coil, is given by changing the sign of  $z$  in  $\gamma_1$ ; and so the complete field at P is

$$\gamma = \gamma_1 + \gamma_2 = \frac{4\pi a^2}{l^3} + \frac{6\pi a^2 z^2}{l^7} (4c^2 - a^2) + \frac{15\pi a^2 z^4}{2l^{11}} (8c^4 - 12a^2 c^2 + a^4),$$

correct as far as terms in  $z^4$ .

So far we have not used the special feature of the Helmholtz arrangement: namely, the relation  $a=2c$ , which provides for the disappearance of the second term in  $\gamma$ .

Inserting this value, we find that on the axis the magnetic field is given by the approximate formula

$$\gamma = \frac{4\pi a^2}{l^3} \left( 1 - \frac{9}{5} \frac{z^4}{l^4} \right) \quad (6)$$

To obtain the field at other points we must calculate first the magnetic potential at P; this is given by

$$-\frac{\partial V}{\partial z} = \gamma,$$

and so, on integrating (6), we find that

$$V = V_0 - \frac{4\pi a^2}{l^2} \left( \frac{z}{l} - \frac{9}{25} \frac{z^5}{l^5} \right) = V_0 - \frac{16\pi}{5} \left( \frac{z}{l} - \frac{9}{25} \frac{z^5}{l^5} \right), \quad (7)$$

where  $V_0$  is the value of  $V$  at O.

Accordingly the value of  $V$  at any other point near O is given by the approximate formula

$$V = V_0 - \frac{16\pi}{5} \left\{ \frac{r}{l} P_1(\cos \theta) - \frac{9}{25} \frac{r^5}{l^5} P_5(\cos \theta) \right\}.$$

As before, we have

$$r P_1(\cos \theta) = z,$$

$$\text{and} \quad r^5 P_5(\cos \theta) = z^5 - 5z^3 \rho^2 + \frac{15}{8} z \rho^4,$$

where

$$\rho = r \sin \theta.$$

Thus the potential is given by the approximation

$$V = V_0 - \frac{16\pi}{5l} z + \frac{18\pi}{125l^3} (8z^3 - 40z^2\rho^2 + 15z\rho^4). \quad (8)$$

Hence the complete field is given by the two components

$$\lambda = \sqrt{(\alpha^2 + \beta^2)} = -\frac{\partial V}{\partial \rho} = \frac{72\pi}{25l^3} z \rho (4z^2 - 3\rho^2) \quad (9)$$

$$\gamma = -\frac{\partial V}{\partial z} = \frac{16\pi}{5l} \left\{ 1 - \frac{9}{5l^2} \left( z^4 - 3z^2\rho^2 + \frac{3}{8}\rho^4 \right) \right\} \quad (10)$$

On remembering that  $l^2 = \frac{5}{4}\alpha^2$ , it will be seen that formulæ (9) and (10) are the same as (C) and (D) of Prof. Nagaoka's paper (*l. c.* p. 387).

### IX. Repulsion Effect between the Poles of an Electric Arc.

To the Editors of the *Philosophical Magazine*.

GENTLEMEN,—

I HAVE read with considerable interest the various theories\* which have been advanced to account for the repulsion effect between the poles of an electric arc. Perhaps you will be good enough to grant me the privilege of suggesting an explanation on somewhat different lines.

Whilst the projection of particles across the gap and the so-called electric wind accompanied by its electrostatic reaction may have an influence on the forces between the electrodes, it seems to me that the "pinch effect" in the arc must also be an important factor. The work of Bary† and Northrup‡ on electromagnetic striction in mobile conductors has left little room for doubt regarding the generality of this phenomenon. The characteristic interruptions and stratification in vacuum-tube discharges, the intermittent current taken

\* A. Sellar, *N. Cimento*, xi. p. 67 (1916) & *Phil. Mag.* (6) xlv. p. 765 (1922). W. G. Duffield, T. H. Burnham, and A. H. Davies, *Roy. Soc. Phil. Trans.* 220. p. 109 (1919). W. G. Duffield and Mary D. Waller, *Phil. Mag.* xl. p. 781 (1920). S. Ratner, *Phil. Mag.* xl. p. 511 (1920). A. M. Tyndall, *Phil. Mag.* xl. p. 780 (1920), & xlii. p. 972 (1921). H. E. G. Beer and A. M. Tyndall, *Phil. Mag.* xlii. p. 956 (1921).

† P. Bary, *L'clairage Electrique*, li. p. 37 (1907); *Lumière Electr.* vi. p. 135 (1909); *Le Radium*, iv. p. 323 (1907); *Journ. de Physique*, viii. p. 190 (1909).

‡ E. F. Northrup, *Phys. Rev.* xxiv. p. 474 (1907).

by mercury-vapour lamps working on a D. C. supply, the singing and whistling arcs, can all be simply explained by this action.

A conductor may be imagined to consist of a large number of filaments parallel to the axis, each carrying part of the total current. All the filaments except the one on the axis will experience a force tending to urge them towards the centre. If, therefore, the conducting column is mobile, it will contract so as to diminish its cross-section and, in consequence, increase in length. If the column cannot increase in length, the hydrostatic pressure will become greater along the axis than near the surface. This conception is easily developed mathematically for a cylindrical conductor. In such a case the intensity of the pressure ( $p$ ) at any radius ( $r$ ) is given by

$$p = \frac{I^2}{\pi R^4} (R^2 - r^2),$$

where  $I$  = total current and  $R$  = external radius of the conductor.

Bary has clearly demonstrated an increase of pressure, towards the axis of a conducting column of gas.

Although a gas will not normally resist change of pressure we have to remember that in the case of an arc the radial striction forces are exerted more or less uniformly along its whole length, so that the ionized vapour is kept within a confined space. The system is analogous to a rubber tube containing gas under pressure and having rigid plugs in its ends. In liquids the contraction is generally more pronounced about midway between the electrodes on account of the relatively large surface friction. In gases the effect will be chiefly a volume change and more uniformly distributed.

If we assume that the conducting column of the arc is cylindrical and contracts uniformly, the force ( $F$ ) on each pole due to the "pinch effect" is obtained by integrating the pressure over the section. For an equilibrium condition it is easy to show that

$$F = \frac{I^2}{2},$$

where  $I$  = total current.

The experimental results obtained by Prof. Duffield suggest that the total force on each electrode, after making proper allowance for the influence of the earth's field and the electrodynamic action of the circuit, is approximately proportional to the square of the current. Moreover, taking a

*Phil. Mag.* Ser. 6. Vol. 46. No. 271. July 1923. I

current of 20 amperes, theoretically we should get about 2 dynes on each pole from this action, which amounts to nearly 30 per cent. of the observed force. It is also significant that the effect is the same for alternating and direct currents.

The researches of Beer and Tyndall on an arc between carbons drilled centrally showed that the hydrostatic pressure is greatest along the axis of the conducting vein.

The observed increased force on the electrodes when an arc is hissing or unsteady might also be expected on the hypothesis that electromagnetic striction is largely responsible. At the moment when the conducting column is ruptured the pressure is very high, and there is a quick projection of the particles to the right and left of the contracted section, producing an increased force on the poles. In some cases the displacement velocity must be very large and the resulting instantaneous pressure correspondingly high. Trotter\* has shown that parts of an arc are in rapid motion during the unstable state when hissing begins.

I suggest that the evidence is in favour of the view that at least a measurable part of the repulsion effect in an arc is due to the "pinch" phenomenon operating in the gaseous conducting column between the poles.

I am, Gentlemen,

Yours faithfully,

H. MONTEAGLE BARLOW.

X. *The Effect of a Steady Wind on the Sea-level near a Straight Shore.* By HAROLD JEFFREYS, M A., D.Sc., Fellow of St. John's College, Cambridge. Being part of a Dissertation commended by the Adjudicators for the Adams Prize, 1923 †.

IT is a well-known result in meteorology that in any steady motion of the atmosphere, apart from the influence of friction, the wind is along the isobars and perpendicular to the horizontal thrust upon it, the higher pressure being on the right in the northern hemisphere, on the left in the southern. The same proposition, subject to the same conditions, must hold in the ocean. It has been shown ‡ that a closely related result holds in the case of ocean currents driven by the

\* Trotter, Proc. Roy. Soc. lvi. p. 262 (1894).

† Communicated by the Author.

‡ Walfrid Ekman, *Arkiv. f. Matematik, Acad. Stockholm*, ii. (1905). Harold Jeffreys, *Phil. Mag.* xxxix. pp. 578-586 (1920).

friction of the wind blowing over the water surface; the resultant drift of the water, if unobstructed in any way, is perpendicular to the wind. The surface current, however, is inclined to the wind towards the high pressure side, and, provided the eddy viscosity is uniform down to a specifiable depth, the inclination is  $45^\circ$ .

It was pointed out to me by Mr. F. J. W. Whipple that this result needs to be modified when the motion is obstructed by a long straight coast, which prevents any resultant drift from taking place across a vertical section parallel to the coast. The modifications required are discussed in this paper. It is found that the ultimate effect of a steady wind is to produce an inclination of the surface of the water, the contour lines being parallel to the coast. The resultant drift in any vertical column is parallel to the coast, but the amounts of the slope and the drift depend on the wind velocity, the depth, and the eddy viscosity. In such a steady motion obstructed by a shore, the current at the surface is not in general at  $45^\circ$  to the wind.

Let the axis of  $x$  be taken parallel to the shore, that of  $y$  at right angles to it, and that of  $z$  vertically downwards. The origin is midway between the undisturbed free surface and the bottom, the latter being assumed horizontal. Let  $n$  be the component of the earth's angular velocity about the downward vertical. The sense of the axes is to be such that  $n$  is positive. Thus if the axis of  $x$  is eastwards, that of  $y$  is towards the nearest pole; and if the axis of  $x$  is towards the equator, that of  $y$  is to the east. With sufficient accuracy  $n$  can usually be treated as a constant.

Let  $p$  be the pressure,  $\rho$  the density,  $k$  the coefficient of eddy viscosity, and  $u$  and  $v$  the components of horizontal velocity. The equations of steady motion of the water are

$$\frac{1}{\rho} \frac{\partial p}{\partial x} = k \frac{\partial^2 u}{\partial z^2} + 2nv, \quad \dots \quad (1)$$

$$\frac{1}{\rho} \frac{\partial p}{\partial y} = k \frac{\partial^2 v}{\partial z^2} - 2nu. \quad \dots \quad (2)$$

Taking a new variable  $w$  equal to  $u + iv$ , we can combine these into the single equation:

$$k \frac{\partial^2 w}{\partial z^2} - 2niw = \frac{1}{\rho} \left( \frac{\partial p}{\partial x} + i \frac{\partial p}{\partial y} \right). \quad \dots \quad (3)$$



If the elevation of the free surface above the undisturbed level is  $\zeta$ , we have :

$$\frac{\partial p}{\partial x} = g\rho \frac{\partial \zeta}{\partial x}; \quad \frac{\partial p}{\partial y} = g\rho \frac{\partial \zeta}{\partial y} \quad \dots \quad (4)$$

We require to know whether a solution is possible, such that all the quantities involved are independent of  $x$ , so that  $\partial p / \partial x$  is zero. With this condition (2) becomes

$$k \frac{\partial^2 w}{\partial z^2} - 2niw = 2niG, \quad \dots \quad (5)$$

where 
$$G = -\frac{g}{2n} \frac{\partial \zeta}{\partial y} \quad \dots \quad (6)$$

On the analogy with the geostrophic wind we may think of  $G$  as the geostrophic current.  $G$  is independent of  $z$ , and therefore the solution of (5) is

$$w = G + A \sinh jqz + B \cosh jqz, \quad \dots \quad (7)$$

where 
$$q^2 = n/k, \quad \dots \quad (8)$$

$$j = 1 + i, \quad \dots \quad (9)$$

and  $A$  and  $B$  are constants. It will be noticed that  $q$  and  $G$  are purely real; but  $A$  and  $B$  may be complex.

Let  $h$  be the depth. There must be no resultant flow across a plane parallel to the shore; for, if there were, water would be accumulating in or disappearing from the neighbourhood of the shore, and the system would not be in a steady state. Hence

$$\int_{-\frac{1}{2}h}^{\frac{1}{2}h} w dz = 0. \quad \dots \quad (10)$$

Neglecting squares of small quantities, we see that  $\int_{-\frac{1}{2}h}^{\frac{1}{2}h} w dz$  is purely real: thus  $\frac{B}{jq} \sinh \frac{1}{2}jqh$  is purely real. If we call this  $C/q$ , and put  $\frac{1}{2}qh = \lambda$ , then (7) takes the form

$$w = G + A \sinh jqz + jC \frac{\cosh jqz}{\sinh j\lambda} \quad \dots \quad (11)$$

Actually the condition in contact with the shore must require the absence of a normal component of velocity at every point: but evidently (10) is all that can be asserted of places remote from the shore. Let the current at the bottom be flowing with speed  $R$  in a direction making the angle  $\gamma$  with the shore line, so that, when  $z = \frac{1}{2}h$ ,

$$w = R e^{i\gamma}. \quad \dots \quad (12)$$

Then 
$$R e^{i\gamma} = A \sinh j\lambda + jC \coth j\lambda + G. \quad \dots \quad (13)$$

The frictional condition for the bottom is

$$-k\rho \frac{\partial w}{\partial z} = 0.002\rho R^2 e^{\gamma}, \quad . \quad . \quad . \quad (14)$$

so that, writing  $\kappa$  for the numerical coefficient 0.002, we have

$$-\frac{\kappa R^2}{k} e^{\gamma} = jqA \cosh j\lambda + j^2 qC. \quad . \quad . \quad . \quad (15)$$

Again, the condition for the free surface is

$$k\rho \frac{\partial w}{\partial z} = -\kappa\sigma Q^2 e^{i\alpha}, \quad . \quad . \quad . \quad (16)$$

where  $Q \cos \alpha$  and  $Q \sin \alpha$  are the component velocities of the wind relative to the water at the surface, and  $\sigma$  is the density of the air. In general, the velocity of the wind is large compared with that of the water, so that  $Q \cos \alpha$  and  $Q \sin \alpha$  may be taken to be the actual components of wind velocity relative to the earth's surface.

Substituting in (16) from (11) we have

$$-\frac{\kappa\sigma}{k} Q^2 e^{i\alpha} = jqA \cosh j\lambda - j^2 qC. \quad . \quad . \quad . \quad (17)$$

Hence from (15) and (17)

$$jqA \cosh j\lambda = -\frac{1}{2} \frac{\kappa}{k} \left( R^2 e^{\gamma} + \frac{\sigma}{\rho} Q^2 e^{i\alpha} \right), \quad . \quad . \quad (18)$$

$$2iqC = -\frac{1}{2} \frac{\kappa}{k} \left( R^2 e^{\gamma} - \frac{\sigma}{\rho} Q^2 e^{i\alpha} \right). \quad . \quad . \quad (19)$$

And from (13)

$$\begin{aligned} G &= Re^{\gamma} + \frac{1}{2} \frac{\kappa}{k} \left( R^2 e^{\gamma} + \frac{\sigma}{\rho} Q^2 e^{i\alpha} \right) \frac{\tanh j\lambda}{jq} \\ &\quad + \frac{1}{2jq} \frac{\kappa}{k} \left( R^2 e^{\gamma} - \frac{\sigma}{\rho} Q^2 e^{i\alpha} \right) \coth j\lambda \\ &= Re^{\gamma} + \frac{\kappa}{qk\sqrt{2}} R^2 \coth 2j\lambda e^{(\gamma - \frac{1}{2}\pi)} \\ &\quad - \frac{\kappa Q^2}{qk\sqrt{2}} \frac{\sigma}{\rho} \operatorname{cosech} 2j\lambda e^{i(\alpha - \frac{1}{2}\pi)}. \quad . \quad . \quad (20) \end{aligned}$$

If  $W$  be the velocity at the surface, we have from (11) and (13)

$$\begin{aligned} W &= Re^{\gamma} - 2A \sinh j\lambda \\ &= Re^{\gamma} + \frac{\kappa}{jkq} \tanh j\lambda \left( R^2 e^{\gamma} + \frac{\sigma}{\rho} Q^2 e^{i\alpha} \right). \quad . \quad (21) \end{aligned}$$

As  $C$  is purely real, equation (19) gives

$$R^2 \cos \gamma - \frac{\sigma}{\rho} Q^2 \cos \alpha = 0. \quad (22)$$

This equation, with those obtained by equating real and imaginary parts in (20), should determine  $G$ ,  $R$ , and  $\gamma$  in terms of  $Q$  and  $\alpha$ . We notice that  $\cos \gamma$  has the same sign as  $\cos \alpha$ ; in other words, the components along the shore of the wind and the bottom drift are in the same direction. Equation (20) can be written

$$G = R e^{i\gamma} + D e^{i(\gamma - \frac{1}{4}\pi)} \frac{\sinh 4\lambda - i \sin 4\lambda}{\cosh 4\lambda - \cos 4\lambda} - E e^{i(\alpha - \frac{1}{4}\pi)} \frac{2(\sinh 2\lambda \cos 2\lambda - i \cosh 2\lambda \sin 2\lambda)}{\cosh 4\lambda - \cos 4\lambda}, \quad (23)$$

where 
$$D = \frac{\kappa R^2}{qk \sqrt{2}} = \frac{\kappa}{qk} \frac{\sigma \cos \alpha}{\sqrt{2} \rho \cos \gamma} Q^2 \quad (24)$$

$$E = \frac{\kappa}{qk} \frac{\sigma}{\sqrt{2} \rho} Q^2 = \frac{\cos \gamma}{\cos \alpha} D. \quad (25)$$

Hence

$$\begin{aligned} & (G - R \cos \gamma) (\cosh 4\lambda - \cos 4\lambda) \\ &= D \{ \cos (\gamma - \tfrac{1}{4}\pi) \sinh 4\lambda + \sin (\gamma - \tfrac{1}{4}\pi) \sin 4\lambda \}, \\ & - 2E \{ \cos (\alpha - \tfrac{1}{4}\pi) \sinh 2\lambda \cos 2\lambda \\ & \quad + \sin (\alpha - \tfrac{1}{4}\pi) \cosh 2\lambda \sin 2\lambda \}, \quad (26) \end{aligned}$$

and

$$\begin{aligned} & -R \sin \gamma (\cosh 4\lambda - \cos 4\lambda) \\ &= D \{ \sin (\gamma - \tfrac{1}{4}\pi) \sinh 4\lambda - \cos (\gamma - \tfrac{1}{4}\pi) \sin 4\lambda \} \\ & - 2E \{ \sin (\alpha - \tfrac{1}{4}\pi) \sinh 2\lambda \cos 2\lambda \\ & \quad - \cos (\alpha - \tfrac{1}{4}\pi) \cosh 2\lambda \sin 2\lambda \}. \quad (27) \end{aligned}$$

Substituting in (27) for  $D$ ,  $E$ , and  $R$  from (22), (24), and (25), we find

$$\begin{aligned} & (\cosh 4\lambda - \cos 4\lambda) \sin \gamma \left( \frac{\rho}{\sigma} \cos \alpha \cos \gamma \right)^{\frac{1}{2}} \frac{qk \sqrt{2}}{\kappa} \\ & + Q \left[ \begin{aligned} & \cos \alpha \{ \sin (\gamma - \tfrac{1}{4}\pi) \sinh 4\lambda - \cos (\gamma - \tfrac{1}{4}\pi) \sin 4\lambda \} \\ & 2 - \cos \gamma \sin (\alpha - \tfrac{1}{4}\pi) \sinh 2\lambda \cos 2\lambda \\ & \quad - \cos (\alpha - \tfrac{1}{4}\pi) \cosh 2\lambda \sin 2\lambda \} \end{aligned} \right] \quad (28) \end{aligned}$$

The square root in this equation arises as  $R \cos \gamma / Q$ , and evidently must have the same sign as  $\cos \gamma$  and  $\cos \alpha$ . The equation (22) should enable us to find  $\gamma$  in terms of  $Q$  and  $\alpha$ ; then (22) should give  $R$ , and finally (26) gives  $G$ . It follows that a steady motion with the contour lines parallel to the shore is in general possible. To make further progress it is necessary to consider special cases, on account of the complexity of the formulæ.

### (1) Case of deep water.

Suppose that  $h$  is so large that  $e^{-2\lambda}$ , which is equal to  $e^{-q^2 h}$ , can be neglected. Then equations (26) and (28) become

$$\sin \gamma \left( \frac{\rho}{\sigma} \cos \alpha \cos \gamma \right)^{\frac{1}{2}} \frac{\sqrt{2nk}}{\kappa} + Q \cos \alpha \sin(\gamma - \frac{1}{4}\pi) = 0; \quad (29)$$

$$G = R \cos \gamma + \frac{\kappa}{\sqrt{2nk}} \frac{\sigma \cos \alpha}{\rho \cos \gamma} Q^2. \quad (30)$$

In these equations the value of  $q$  from (8) has been substituted. Substituting in (30) for  $R$  and  $Q$  in terms of  $\gamma$  from (22) and (29), we find

$$G = \frac{2 \sqrt{nk}}{\kappa} \frac{\sin \gamma}{1 - \sin 2\gamma}. \quad (31)$$

Equation (29) can be written :

$$\frac{\sin^2 \gamma \cos \gamma}{1 - \sin 2\gamma} = \frac{\sigma}{\rho} \frac{\kappa^2}{4nk} Q^2 \cos \alpha. \quad (32)$$

Hence 
$$G = \frac{\kappa}{2 \sqrt{nk}} \frac{\sigma}{\rho} \frac{Q^2 \cos \alpha}{\sin \gamma \cos \gamma}. \quad (33)$$

We see from (29) that  $\sin \gamma$  and  $\sin(\gamma - \frac{1}{4}\pi)$  must have opposite signs. Hence  $\gamma$  lies between 0 and  $\frac{1}{4}\pi$  or between  $\pi$  and  $\frac{5}{4}\pi$ . Remembering that  $\cos \alpha$  and  $\cos \gamma$  have the same sign, we see, therefore, that if  $\cos \alpha$  is positive,  $\gamma$  lies between 0 and  $\frac{1}{4}\pi$ , and if  $\cos \alpha$  is negative,  $\gamma$  lies between  $\pi$  and  $\frac{5}{4}\pi$ . Accordingly in the northern hemisphere, with a coast running east and west, if the wind has a component from the east, the bottom drift is towards some direction between W. and S.W.; if the wind has a component from the west, the bottom drift is towards a direction between E. and N.E. These results hold whether the other component of the wind is from the north or the south.

When  $\gamma$  increases from 0 to  $\frac{1}{2}\pi$ ,  $\frac{\sin^2 \gamma \cos \gamma}{1 - \sin 2\gamma}$  increases steadily from 0 to  $+\infty$ . Hence for every positive value of the quantity on the right of (32) there is one possible value of  $\gamma$ . The same is easily seen to hold for negative values. We also see that small values of  $Q^2 \cos \alpha$  correspond to small values of  $\gamma$ , while large values of  $Q^2 \cos \alpha$  correspond to values of  $\gamma$  near  $\frac{1}{2}\pi$ . Hence by (22) and (31)  $R$  and  $G$  tend to zero with  $Q^2 \cos \alpha$ . A wind at right angles to the shore therefore produces no drift of the water in deep water. This agrees with previous results. In the open ocean the resultant momentum relative to the earth's surface should be at right angles to the wind, and therefore a shore at right angles to the wind should not interfere with it. A gentle wind tends to produce a general drift of the water parallel to the shore: a stronger wind at the same inclination to the shore causes the bottom drift to be markedly inclined to the shore.

#### *Deep water: Numerical Examples.*

In an ordinary case we may have  $\rho = 800\sigma$ ,  $n = 8 \times 10^{-5}/\text{sec.}$ ,  $k = 100 \text{ cm.}^2/\text{sec.}$  If the wind attains the gale velocity of 18 m./s., with  $\cos \alpha = 1$ , the quantity on the right of (32) is nearly  $\frac{1}{2}$ . Accordingly, for strong gales and hurricanes nearly parallel to the coast, we can treat it as large, but for lighter winds and gales nearly at right angles to the coast it is small. In the former case  $\gamma = \frac{1}{2}\pi$  nearly, and in the latter  $\gamma$  is small.

(a) Hurricanes alongshore. Equation (33) reduces nearly to

$$G = \frac{\kappa}{2\sqrt{(nk)}} \frac{\sigma}{\rho} Q^2 \cos \alpha, \quad . \quad . \quad . \quad (34)$$

and if  $Q$  is 40 m./s. we find that  $G$  is 4 m./s. Then

$$\frac{\partial \xi}{\partial y} = - \frac{2nG}{g} = - \frac{6 \text{ cm.}}{1 \text{ km.}}$$

Thus if such a wind was from the north, the water level along an eastern shore would be higher by 24 m. than that at an opposite shore 400 km. away.

The approximations of this paragraph are also the conditions that the square terms in (21) shall be great compared with  $Re^\gamma$ ; also  $\tanh j\lambda$  is approximately unity.

Hence, to this accuracy,

$$W = \frac{\kappa}{\sqrt{(2nk)}} \frac{\sigma}{\rho} Q^2 e^{-\frac{1}{2}\pi} \left( e^{i\gamma} \frac{\cos \alpha}{\cos \gamma} + e^{i\alpha} \right) \\ = \frac{\kappa}{\sqrt{(2nk)}} \frac{\sigma}{\rho} \frac{Q^2 e^{-\frac{1}{2}\pi}}{\cos \gamma} \{ 2 \cos \alpha \cos \gamma + i \sin (\alpha + \gamma) \}. \quad (35)$$

Substituting for  $\gamma$  we get

$$W = \frac{\kappa}{\sqrt{(2nk)}} \frac{\sigma}{\rho} Q^2 e^{-\frac{1}{2}\pi} \{ 2 \cos \alpha + i \cos \alpha + i \sin \alpha \}. \quad (36)$$

If the inclination of the surface-drift to the coast is  $\beta$ , we have

$$\beta = -\frac{1}{4}\pi + \tan^{-1} \frac{1}{2}(1 + \tan \alpha) \\ \tan \beta = \frac{\tan \alpha - 1}{\tan \alpha + 3}. \quad (37)$$

If  $\alpha = 0$ , corresponding to a wind parallel to the shore,  $\tan \beta = -\frac{1}{3}$ , so that  $\beta = -18^\circ$ . The surface-drift is therefore inclined towards the shore to the right of the wind, but at a smaller inclination than in the absence of any obstruction.

If  $\alpha = \frac{1}{2}\pi$ ,  $\beta = \frac{1}{4}\pi$ , so that the surface-drift is at  $45^\circ$  to the wind. This is what we should expect, since this is the case where the coast does not interfere with the general drift.

(b) Light to strong wind alongshore, or gale nearly at right angles to the shore.

Here the quantity on the right of (32) is small, so that  $\gamma$  is small. We have then

$$\sin \gamma = Q \cos^{\frac{1}{2}} \alpha \left( \frac{\sigma}{\rho} \right)^{\frac{1}{2}} \frac{\kappa}{2(nk)^{\frac{1}{2}}}. \quad (38)$$

$$G = \left( \frac{\sigma}{\rho} \right)^{\frac{1}{2}} Q \cos^{\frac{1}{2}} \alpha. \quad (39)$$

Thus if  $Q \cos^{\frac{1}{2}} \alpha = 5$  m./s.,  $G = 18$  cm./sec.,

and  $\frac{\partial \zeta}{\partial y} = - \frac{0.3 \text{ cm.}}{1 \text{ km.}}$

Such a wind would therefore produce a difference of level of 1.2 metres between points at the shore and 400 km. from it.

The first term in (21) is large in this case compared with the square terms, so that

$$W = Re^{i\gamma} = G, \quad (40)$$

and as  $\gamma = 0$ , approximately, we see that the surface-drift caused by a light wind is parallel to the shore.

## (2) Case of shallow water.

Suppose that  $h$  is so small that  $\lambda^2$ , which is equal to  $\frac{1}{4}q^2h^2$ , can be neglected. The most convenient way of dealing with this case is to return to equation (20).

$$G - Re^{\gamma} = De^{i(\gamma - \frac{1}{2}\pi)} \coth 2j\lambda - Ee^{i(\alpha - \frac{1}{2}\pi)} \operatorname{cosech} 2j\lambda. \quad (41)$$

Remembering that  $e^{-i\frac{1}{2}\pi} = \sqrt{2}/j$ , and  $j^2 = 2i$ ,  $q^2 = n/k$ ,

$$E = \frac{\kappa Q^2}{qk \sqrt{2}}, \quad D = E \frac{\cos \alpha}{\cos \gamma},$$

we readily transform this to

$$G - Re^{\gamma} = \frac{\kappa Q^2}{2nk} \frac{\sigma \sin(\alpha - \gamma)}{\rho \cos \gamma}. \quad (42)$$

Equating imaginary parts in this equation, we see that

$$R \sin \gamma = 0,$$

and therefore  $\gamma$  is zero or  $\pi$ , and the bottom drift is parallel to the shore. Equations (22) and (42) therefore reduce to

$$R^2 = \frac{\sigma}{\rho} Q^2 \cos \alpha,$$

$$G = R - \frac{\kappa Q^2}{2nh} \frac{\sigma}{\rho} \sin \alpha. \quad (43)$$

$$= R - \frac{\kappa R^2}{2nh} \tan \alpha. \quad (44)$$

It will be noticed that  $k$  is not explicitly involved in these equations, so that the results obtained for shallow water do not depend on the eddy-viscosity, provided that this is such that the approximation is valid.

If  $k = 100 \text{ cm.}^2/\text{sec.}$ ,  $n = 10^{-3}/\text{sec.}$ , the condition for this is that  $\frac{1}{2}h\sqrt{(n/k)}$  is small, which requires that  $h$  shall be small compared with 60 metres. Suppose now that  $Q = 10 \text{ m./s.}$ , and that  $\alpha = \frac{1}{4}\pi$ . Then  $R = 60 \text{ cm./sec.}$  by (43), and the second term in (44) will be large compared with the first, provided that  $h$  is small compared with 60 metres. Hence the condition that we can approximate to (41) by neglecting positive powers of  $\lambda$  implies the condition that we can neglect the first term in (44), provided the wind exceeds  $10 \text{ m./s.}$ , and we have therefore with sufficient accuracy

$$G = - \frac{\kappa Q^2}{2nh} \frac{\sigma}{\rho} \sin \alpha, \quad (45)$$

and

$$\begin{aligned} \frac{\partial \zeta}{\partial y} &= - \frac{2nG}{g} \\ &= \frac{\kappa Q^2}{gh} \frac{\sigma}{\rho} \sin \alpha. \end{aligned} \quad (46)$$

These results are strikingly different from the corresponding equations (34) and (39) for deep water. In fact, when  $\alpha$  is zero, the wind produces no slope of the surface in the case just discussed. On the other hand, in deep water the maximum slope is produced by a wind parallel to the shore, and no slope is produced by a wind at right angles to the shore. In shallow water the maximum slope is produced by a wind at right angles to the shore, and no slope is produced by a wind parallel to the shore.

In the shallow water case equation (21) reduces to

$$W = Re^{\gamma} + \frac{1}{2} \frac{\kappa h}{k} \left( R^2 e^{\gamma} + \frac{\sigma}{\rho} Q^2 e^{i\alpha} \right),$$

$$= R + \frac{1}{2} \frac{\kappa h}{k} R^2 (2 + i \tan \alpha). \quad (47)$$

The eddy viscosity is therefore explicitly involved in the surface-drift, which takes place at an inclination to the shore intermediate between 0 and  $\tan^{-1}(\frac{1}{2} \tan \alpha)$ , approximating to the former value for light winds and to the latter for strong winds.

If we have  $Q = 10$  m./s.,  $h = 10$  m., and  $\alpha = \frac{1}{4}\pi$ , (46) gives

$$\frac{\partial \zeta}{\partial y} = -\frac{1}{6} \frac{\text{cm.}}{\text{km.}},$$

and if  $k = 100$  cm.<sup>2</sup>/sec.,

$$W = (48 + 9i) \text{ cm./sec.}$$

Thus the surface-drift has a resultant velocity of about 49 cm./sec., inclined at  $10^\circ 30'$  to the shore.

It may be noticed that if the friction of the wind on the water surface is redistributed uniformly through the depth of the water, the force per unit mass in the direction of  $y$  is  $\frac{\kappa \sigma Q^2 \sin \alpha}{\rho h}$ , and the equation of motion at right angles to the coast, internal and bottom friction being neglected, is

$$\frac{\partial v}{\partial t} + 2nu = \frac{\kappa \sigma Q^2 \sin \alpha}{\rho h} - \frac{g}{\rho} \frac{\partial \zeta}{\partial y}.$$

When we give  $\frac{\partial \zeta}{\partial y}$  the value found in (41), the right side vanishes. Hence the slope of the surface in the case of shallow water is the same as that of an equilibrium tide unaffected by internal and bottom friction and with the skin friction at the surface uniformly distributed through the depth.



## 124 *Effect of Steady Wind on Sea-level near Straight Shore.*

*The time needed to establish the steady state.*

Let us consider the conditions in the open ocean, with no complication arising from the slope of the free surface. The force per unit area acting across the surface is  $\kappa\sigma Q^2$  in the direction of the wind. When a steady state is attained, which will ordinarily take about a day, the momentum relative to the solid earth of a vertical column of water of unit cross-section will therefore be  $\kappa\sigma Q^2/2n$ , at right angles to the wind. Accordingly, if we consider a surface inclined at an angle  $\alpha$  to the wind, the volume of water crossing it in unit time will be  $\kappa\sigma Q^2 \cos \alpha / 2n\rho$  per unit length.

Now suppose that parallel to such a surface, at a distance  $l$ , a solid vertical barrier is suddenly inserted. The water will temporarily cross the surface considered at the same rate as before, but clearly this cannot be maintained, for in time enough water will have crossed to raise or lower the slope of the surface to the value found in the case of a steady motion obstructed by a shore, and further accumulation will not take place. To raise the slope to the equilibrium value  $\frac{\partial \zeta}{\partial y}$ , the amount of water required is evidently  $\frac{1}{2}l^2 \frac{\partial \zeta}{\partial y}$  per unit length. Hence the time taken to establish a steady slope within a distance  $l$  of the coast must be of order

$$\frac{n\rho l^2}{\kappa\sigma Q \cos \alpha} \frac{\partial \zeta}{\partial y} \quad \text{or} \quad \frac{2n^2\rho l^2 G}{\kappa g \sigma Q^2 \cos \alpha}, \quad \text{by (9)}$$

In the case of a hurricane blowing over deep water, this reduces, by (34), to  $\frac{n^2 l^2}{g k^{\frac{1}{2}}}$ . If  $l = 2 \times 10^7$  cm. = 200 km.,  $n = 4 \times 10^{-5}$ /sec.,  $g = 980$  cm./sec.<sup>2</sup>, and  $k = 100$  cm.<sup>2</sup>/sec., this is practically  $10^4$  secs. or 3 hours. Accordingly the steady conditions will be established within 200 km. of the shore in a few hours.

In the case of a light wind over deep water, the time required reduces, by (39), to  $\frac{2n^2 l^2}{\kappa g G}$ . With our previous data and  $G = 18$  cm./sec., as on p. 121, paragraph (b), this is about 12 hours.

In the shallow water case, equation (45) gives the time as  $n^2 \tan \alpha / gh$ . With the previous data and  $h = 10$  metres, this becomes 16,000 secs., or  $4\frac{1}{2}$  hours.

The time needed to convert open ocean conditions into a state of steady motion obstructed by a shore is therefore a fraction of a day for places within 200 km. of the coast. The time required to establish such conditions at greater distances from the shore is proportional to the square of the

distance. In general a steady motion in a confined sea will be established in a day from the commencement of the wind.

The motion of water in the open ocean under the influence of a cyclone or a large seasonal depression or elevation may be discussed on these lines. The drift is at right angles to the wind, towards the high pressure side, and therefore tends to lower the water-surface within the cyclone. (The direct effect of pressure on the water-surface is, of course, in the opposite sense, but is not part of the subject-matter of this paper.) The argument of the papers quoted on p. 114 applies to cases where the surface has no slope, and therefore only to the early stages of the disturbances. The conditions are, in general, those of light winds over deep water, and we see that the surface-current will be at  $45^\circ$  to the wind in the early stages, becoming more nearly along the isobars in the latter stages. For a cyclone with light winds and with horizontal dimensions large compared with 400 km., the time taken for the change will be of order 3 or 4 days; for a hurricane we have already seen that it is a few hours; and for a disturbance whose horizontal dimensions are large compared with 4000 km., the time is a few months. Hence in seasonal disturbances in the Pacific and Atlantic Oceans the surface-current should be at approximately  $45^\circ$  to the wind.

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XI. *The Stress System of the Four-Dimensional Electromagnetic Field.* By S. R. MILNER, D.Sc., F.R.S., Professor of Physics, The University, Sheffield\*.

IN certain respects, as has been shown in a recent paper †, the general electromagnetic field, when it is considered as a four-dimensional entity, appears as the exact and natural extension to four dimensions of the three-dimensional electrostatic field. In the latter the properties are expressed in terms of a vector function of position  $\mathbf{e}$  "acting" in a certain line, say  $x$ , the orientation of which, along with that of the plane  $yz$ , to which it is perpendicular, is fixed for each point. In the electromagnetic field in four dimensions the properties may be expressed by a vector function of position

$$R = \{(\mathbf{e}^2 - \mathbf{h}^2)^2 + 4(\mathbf{e} \cdot \mathbf{h})^2\}^{1/4}$$

"acting" in a certain plane, say  $xt$ , the orientation of which, along with that of the plane  $yz$  to which it is perpendicular, is fixed for each point. In the one case the fundamental electrostatic equations are equivalent to the statement that the vector  $\mathbf{e}$  can be represented by lines of force, or in

\* Communicated by the Author.

† Milner, Phil. Mag. xlv. p. 705 (1922).

other words that the flux of  $\mathbf{e}$  over the cross-section of a Faraday tube is constant throughout its length. In the other the fundamental electromagnetic equations are equivalent to the same statement with respect to the vector  $\mathbf{R}$ .

There is of course a difference between the two fields which is obvious to the senses and which is due to the fact that geometry in the  $t$  direction is different in character from the geometry of the  $xyz$  space. By using imaginary time  $l=it$  the difference of the geometries disappears and the equivalence of the two fields is rendered complete, at any rate in these respects.

The stress system of a four-dimensional electromagnetic field forms another respect in which a similar exact equivalence holds with an electrostatic field in three dimensions. Every element of the latter may be regarded as being in equilibrium under the action of a tension of magnitude  $\frac{1}{2}e^2$  along the lines of force combined with an equal pressure at right angles to them. This stress system may be represented with arbitrary axes  $x, y, z$ , as a tensor

$$\left. \begin{aligned} P_{xx} &= \frac{1}{2}(-e_x^2 + e_y^2 + e_z^2), & P_{xy} &= P_{yx} = -e_x e_y, \\ P_{yy} &= \frac{1}{2}(-e_y^2 + e_z^2 + e_x^2), & P_{yz} &= P_{zy} = -e_y e_z, \\ P_{zz} &= \frac{1}{2}(-e_z^2 + e_x^2 + e_y^2), & P_{zx} &= P_{xz} = -e_z e_x. \end{aligned} \right\} \dots (1)$$

Here  $P_x$  represents the vector stress on a unit area of the plane  $yz$  whose normal is the  $x$  axis, and  $P_{xx}, P_{xy}, P_{xz}$  are the components of  $P_x$  along  $x, y, z$ . To see the equivalence of (1) with the stress system as described, choose the axes so that

$$e_x = e, \quad e_y = e_z = 0.$$

We get

$$P_{xx} = -\frac{1}{2}e^2, \quad P_{yy} = P_{zz} = +\frac{1}{2}e^2, \quad P_{xy} = 0, \text{ etc.}$$

The components along the axes of  $\mathbf{F}$ , the resultant force per unit volume acting on an element  $dx dy dz$  of the field, are given by

$$F_x = \frac{\partial P_{xx}}{\partial x} + \frac{\partial P_{yx}}{\partial y} + \frac{\partial P_{zx}}{\partial z}, \text{ etc.}$$

The equilibrium of the stress follows from the fact that, as a result of the fundamental electrostatic equations ( $\text{curl } \mathbf{e} = 0$ ,  $\text{div } \mathbf{e} = 0$ ) each component of  $\mathbf{F}$  reduces to zero.

Consider now in the general electromagnetic field in four dimensions the following tensor, which has been given by Sommerfeld (*Ann. d. Phys.* xxxii. p. 769, 1910) as the most general symmetrical tensor product determinable from the two six-vectors of the electromagnetic field  $(\mathbf{h}, -i\mathbf{e}), (-i\mathbf{e}, \mathbf{h})$ .

$$\left. \begin{aligned} P_{xx} &= \frac{1}{2}(-e_x^2 + e_y^2 + e_z^2 - h_x^2 + h_y^2 + h_z^2), \\ P_{yy} &= \frac{1}{2}(-e_y^2 + e_z^2 + e_x^2 - h_y^2 + h_z^2 + h_x^2), \\ P_{zz} &= \frac{1}{2}(-e_z^2 + e_x^2 + e_y^2 - h_z^2 + h_x^2 + h_y^2), \\ P_{ll} &= \frac{1}{2}(-e_x^2 - e_y^2 - e_z^2 - h_x^2 - h_y^2 - h_z^2); \\ P_{xy} &= P_{yx} = -(e_x e_y + h_x h_y), \\ P_{yz} &= P_{zy} = -(e_y e_z + h_y h_z), \\ P_{zx} &= P_{xz} = -(e_z e_x + h_z h_x); \\ P_{xl} &= P_{lx} = -i(e_x h_y - e_y h_x), \\ P_{yl} &= P_{ly} = -i(e_y h_z - e_z h_y), \\ P_{zl} &= P_{lz} = -i(e_z h_x - e_x h_z). \end{aligned} \right\} \quad (2)$$

This may be interpreted as a four-dimensional stress, where  $P_x$  stands for the four vector stress on a unit volume of the hyperplane  $yzl$  whose normal is the  $x$  axis, and  $P_{xx}$ ,  $P_{xy}$ ,  $P_{xz}$ ,  $P_{xl}$  are the components of  $P_x$  along  $x$ ,  $y$ ,  $z$ ,  $l$ . The components along the four axes of the resultant force per unit hypervolume on an element  $dx dy dz dl$  are then given by the equations

$$\begin{aligned} F_x &= \frac{\partial P_{xx}}{\partial x} + \frac{\partial P_{yx}}{\partial y} + \frac{\partial P_{zx}}{\partial z} + \frac{\partial P_{lx}}{\partial l}, \\ F_y &= \frac{\partial P_{xy}}{\partial x} + \frac{\partial P_{yy}}{\partial y} + \frac{\partial P_{zy}}{\partial z} + \frac{\partial P_{ly}}{\partial l}, \\ F_z &= \frac{\partial P_{xz}}{\partial x} + \frac{\partial P_{yz}}{\partial y} + \frac{\partial P_{zz}}{\partial z} + \frac{\partial P_{lz}}{\partial l}, \\ F_l &= \frac{\partial P_{xl}}{\partial x} + \frac{\partial P_{yl}}{\partial y} + \frac{\partial P_{zl}}{\partial z} + \frac{\partial P_{ll}}{\partial l}. \end{aligned}$$

For simplicity we confine the discussion to regions where there is no electric charge. As a result of the fundamental electromagnetic equations each component of  $F$  reduces to zero, so the element is subject to no resultant force. There is no torque also, in consequence of the equality of  $P_{xy}$  with  $P_{yx}$ , etc. It follows that the general electromagnetic field in hyperspace with imaginary time may be looked upon as being in static equilibrium under the action of the stress system (2)\*.

\* This is not put forward as a new result, but I have not seen it stated anywhere in this form. It is of course only by representing time as imaginary space that the complete symmetry of  $l$  with  $x$ ,  $y$ ,  $z$  appears. With real time the equations  $F_x=0$ , etc., are expressions of well-known theorems, the first three that the time-rate of increase of the momentum of a space element of the field is equal to the resultant of Maxwell's

To see the real meaning of the stress tensor (2), its expression can be simplified by changing the axes in precisely the same way as the three-dimensional stress tensor was simplified. The possibility of this follows from a proposition which was proved in the previous paper: "In the general electromagnetic field in four dimensions it is always possible to choose the axes of  $x, y, z$ , and  $l$  at any point in such directions that the electric and magnetic forces are collinear and along the direction of  $x^*$ ."

If we then choose the axes so that this condition is satisfied, *i. e.* so that

$$e_x = E, \quad h_x = H, \quad e_y = e_z = h_y = h_z = 0,$$

the expression for the Sommerfeld tensor (2) becomes

$$P_{xx} = P_{ll} = -\frac{1}{2}(E^2 + H^2) = -\frac{1}{2}R^2,$$

$$P_{yy} = P_{zz} = +\frac{1}{2}(E^2 + H^2) = +\frac{1}{2}R^2,$$

with all the remaining components zero.

The tensor (2) consequently represents a stress system consisting of a tension of  $\frac{1}{2}R^2$  in all directions in the  $xl$  plane of these axes, combined with an equal pressure in all directions of the absolutely orthogonal  $yz$  plane. This is an exact extension to four dimensions of the electrostatic stress system in three. The five-vector  $(R, iR)$  (six-vector with its two parts equal) consists of  $R$  associated with the  $yz$  plane by "acting" along every direction in the  $xl$  plane perpendicular to  $yz$ , combined with  $iR$  similarly associated with the  $xl$  plane. It is the natural extension to four dimensions of the vector  $\mathbf{e}$  in the three-dimensional electrostatic system. In the four-dimensional system half the square of the vector in each case gives the stress over the corresponding plane (*i. e.*  $\frac{1}{2}R^2$  over  $yz$ , and  $\frac{1}{2}(iR)^2$  over  $xl$ ). There is here a complete symmetry of the tensions and pressures, as against only a partial symmetry in the three-dimensional case.

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electromagnetic stress on it, and the fourth that the rate of increase of the energy density at a point is equal to the convergence there of Poynting's energy flux. But even with real time the equations may also be looked on as the expression of the static equilibrium of a four-dimensional system of stress, the formulæ being direct extensions of those of the three-dimensional system when allowance is made for the different geometry of hyperspace in the  $t$  direction. The result is consequently implicitly contained in the formulæ for the tensor in the general relativity theory. (See Eddington, 'Mathematical Theory of Relativity,' p. 182 (1923), where the general properties of the tensor are discussed.)

\* Choosing the  $l$ -axis is equivalent to transforming the field for an arbitrary velocity of the observer. To produce collinearity of  $\mathbf{e}$  and  $\mathbf{h}$ , strictly speaking only the absolutely orthogonal planes  $xl$  and  $yz$  need be fixed.

**XII. The Emission of Secondary Electrons from Metals under Electronic Bombardment.** By FRANK HORTON, *Sc.D.*, *F.R.S.*, and ANN CATHERINE DAVIES, *D.Sc.\**.

**I**N the *Philosophical Magazine* for May 1923, Mr. E. W. B. Gill has criticised certain statements made by the writers in a paper describing the results of an investigation of the effects of electron collisions with platinum and with hydrogen†. The main object of this investigation was to test whether the secondary emission of electrons obtained by the electronic bombardment of platinum could be attributed to ionization of hydrogen occluded in the surface of the metal. In the introduction to the paper, the summary given by Campbell‡ of the work of Lenard, Baeyer, Gehrts, etc., and of Campbell himself, is referred to, and the views then prevailing with regard to reflexion and secondary emission are stated. As a preliminary to our main investigation, a few series of observations were taken of the current to the bombarded platinum plate with gradually increasing values of the velocity of impact of the primary electrons, using a constant difference of potential between the glowing filament which was the source of the primary electrons and the grid on which the electrons leaving the plate were collected. A curve representing a typical series of observations is given in the paper, and the various parts of this curve are there interpreted in accordance with the conclusions established by other workers.

Mr. Gill has performed some experiments with an apparatus differing in several important respects from that employed by us, and the results of these experiments have led him to criticise the interpretation which we put upon the various parts of the curve already referred to. These criticisms do not affect the main conclusions of our investigation into the origin of the ionization which occurs at the platinum surface under the electronic bombardment, for the proof of the occurrence of this ionization was the detection, under suitable conditions, of positive ions leaving the plate. As, however, we are unable to admit the applicability of Mr. Gill's contentions to experiments made with the apparatus and arrangements employed by us, it is perhaps desirable that his statements should not be allowed to pass unanswered.

The criticisms fall into two main divisions:—

(a) Those based on the argument that experiments such

\* Communicated by the Authors.

† F. Horton and A. C. Davies, *Proc. Roy. Soc. A.* vol. xcvii. p. 23 (1920).

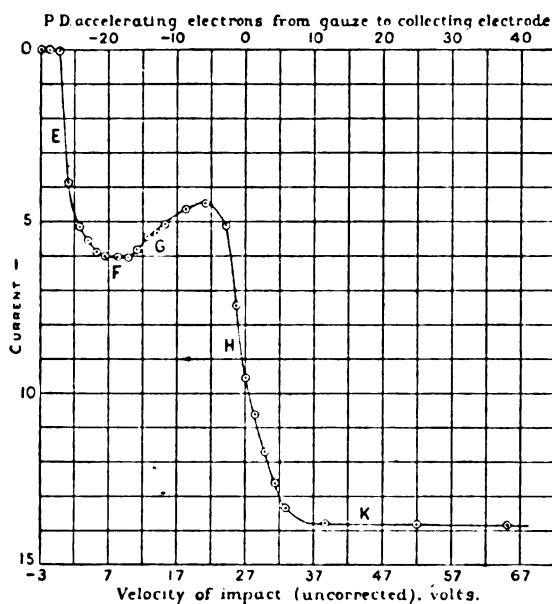
‡ N. R. Campbell, *Phil. Mag.* vol. xxv. p. 803 (1913).  
*Phil. Mag.* S. 6. Vol. 46. No. 271. July 1923.

as those of which the results are represented by our plate current-velocity of impact curve are incapable of discriminating between reflexion and secondary emission, or of enabling the critical voltages for the beginning of these effects to be determined with accuracy.

(*l*) Those based on the argument that a considerable error is introduced by assuming that the electric fields on either side of the grid are independent of each other.

With regard to (*a*) the authors did not claim that the experiments criticised did distinguish between the reflexion

Fig. 1.



Curve representing the variation of the current measured by the electrometer connected to the plate, as the velocity of impact of the primary electron stream is gradually raised. [Reduced from the figure in the Proceedings of the Royal Society, vol. xcvii.]

of the primary electrons and a genuine secondary emission, but merely that their results could be logically interpreted in accordance with the views current at the time. They do, however, still hold the view that the sharpness of the bend between the parts F and G of the curve in question (which, for convenience of reference, is reproduced here) indicates the commencement of a new effect when the velocity of impact reaches the value which it has at the point of inflexion.

The sharpness of this bend is not shown in the inaccurate reproduction of the curve given in Mr. Gill's paper. That the occurrence of an inflexion at this particular velocity of impact is significant, and not, as Mr. Gill suggests, fortuitous, is supported by the fact that with a suitable arrangement of electric fields, positive ions could first be detected leaving the bombarded plate when the velocity of impact of the primary electrons reached this particular value. The conclusion that there is a definite velocity of impact at which the true secondary emission of electrons from a bombarded metal surface begins, is supported by the results of the recent experiments of H. E. Farnsworth\* on the electronic bombardment of nickel. In these experiments the electrons leaving the bombarded nickel plate were collected on an independent conductor, and it was found that at about 9 volts velocity of impact the ratio of the current leaving the nickel plate to the primary current began to increase rapidly. Moreover, by separate experiments it was shown that the distribution of velocities among the electrons leaving the plate changed abruptly at this same velocity of impact in the manner to be expected if a genuine secondary emission were beginning.

With regard to the criticism (b) :—Mr. Gill's experiments were made with a three-electrode Marconi valve, which does not appear to the authors to have been suitable for investigating the emission of secondary electrons from a metal under electronic bombardment. The grid and plate of the valve used were coaxial cylinders with the filament as axis. The grid had a square mesh of side about 1.5 mm. and the open ends were 1 cm. in diameter, the diameter of the cylindrical anode being 2.5 cm. The effects of the size of the grid mesh and of the open ends of a cylindrical grid occupied the attention of the authors in connexion with the design of a thermionic valve in the early days of the war, and they agree with Mr. Gill that, with such an arrangement as he employed, when the potential of the grid ( $V_g$ ) is kept constant and that of the plate is increased, there may be a marked increase in the proportion of the electrons leaving the filament which reach the plate owing to the imperfect shielding action of the grid.

The apparatus used by the authors was constructed so as to avoid errors due to incomplete screening of the various electric fields from each other. The filament was enclosed in a platinum cylinder through a small hole in the centre of the top of which the electrons which formed the primary

\* H. E. Farnsworth, Proc. Nat. Acad. Sci. vol. viii. p. 251 (1922).



bombarding stream were emitted. The stream was prevented from spreading laterally (and so introducing complications) by means of a strong magnetic field at right angles to the electrodes. The platinum gauze which was used as the grid was of fine mesh, the spaces being 0.0526 sq. mm. in area (or only about one-fortieth of the area of the spaces in Mr. Gill's grid), and the width of the wires of the gauze used was about one-third of the distance separating them. Moreover, the gauze formed the base of a platinum cylinder which enclosed the platinum plate, the arrangement (a diagram of which is given in our paper) being such that no electrons from the filament could have reached the plate without passing through the gauze, even if the magnetic field had not been used to keep the stream central in the tube. With such an apparatus it is obvious that any defect in the screening action of the grid is very much smaller than in the case of the valve used by Mr. Gill.

Let us now consider Mr. Gill's criticism of our statement in regard to the large increase of negative current which is indicated by the part H of the curve reproduced. It will be seen that as the potential difference between the gauze and the plate (the collecting electrode) was gradually raised, the negative current to the plate began to increase while this electrode was still about 5 volts negative to the grid. This increase of negative current was attributed by the authors to a decrease in the number of secondary electrons leaving the bombarded plate rather than to an increase in the number of primary electrons reaching it. Mr. Gill accuses the authors of having evaded an explanation of this "difficulty," and makes the statement that, if the field between the grid and the plate were determined simply by the applied potentials, it would certainly remove the electrons to the grid as long as  $V_p$  was less than  $V_g$ . The authors were not aware that the phenomenon presented any difficulty of interpretation, for it seemed to them not at all improbable that a difference of potential of a few volts would be required between the plate and the grid in order to cause the current due to the secondary electrons liberated at the plate to attain its saturation value. The surface of the plate is not perfectly smooth, and the holes in it (of molecular dimensions) serve to screen many of the emitted electrons from the action of the field, so that a potential difference (of about 5 volts in the curve reproduced) was required to drive all of these electrons to the grid.

Mr. Gill seeks to explain the phenomenon in another way, as being due to the field near our plate becoming zero and

reversing before the value of  $V_p$  reaches that of  $V_g$  (presumably 5 volts before this equality is established), and he refers to Maxwell's investigation of the theory of a grating of parallel wires\*. Dr. Appleton, of the Cavendish Laboratory, who has made an extensive investigation of the screening action of grids, observing this fallacy in Mr. Gill's interpretation, was good enough to inform the authors that in an apparatus of the form used by them the shielding must have been almost complete, and that the direction of the field near the plate could not have reversed until  $(V_g - V_p)$  became a very small fraction of  $V_p$ . In Maxwell's investigation, to which Mr. Gill refers, the case considered is that of a grating of parallel wires between two parallel plane electrodes, the grating being thus similarly situated to the platinum gauze in our experiments. If one considers the wires in one direction only in our gauze and applies Maxwell's formula to the case, one obtains the result that the surface density of the electrification on the plate becomes zero when  $(V_g - V_p)$  is about  $\frac{1}{300}$  of  $V_p$ . The shielding of the actual grid is, of course, more nearly perfect than this because of the cross-wires, at right angles to the wires considered, which form another similar grating. It will thus be seen that in the series of observations represented by our curve, the difference of potential between the grid and the plate when the direction of the field near the plate changed sign cannot possibly have been as much as  $\frac{1}{10}$  of a volt—the limit of accuracy claimed by us for the results of experiments of this nature. Thus the increase of negative current beginning while the grid was still about 5 volts positive to the plate cannot have been due to the cause suggested by Mr. Gill.

It may here be stated that the magnitude of the difference of potential between the grid and the plate at which the direction of the field reverses may be investigated experimentally by observations on the direction of the resultant photoelectric current with small applied differences of potential between these electrodes, while a strong constant field is maintained on the other side of the grid. Such an investigation had convinced the authors that any deficiency of the shielding action of the grids used by them was negligible in the circumstances in which these grids were employed.

The proof that the shielding action of the grid was almost perfect disposes of Mr. Gill's contention that, because the authors made no allowance for an increase, with increasing plate potential, of the primary current to the plate at the

\* 'Electricity and Magnetism,' vol. i. 3rd edn. p. 312.

expense of the primary current to the grid, their estimate of about 9 volts as the equivalent velocity of emission of the fastest secondary electrons is unreliable, and its agreement with the results of Lenard and others accidental. It should perhaps be mentioned that Farnsworth, in the recent experiments already referred to, obtained evidence of the presence among the electrons leaving the bombarded plate of a small percentage of electrons having velocities nearly up to that of the primary stream. Farnsworth concluded that these electrons were reflected from the plate and did not form part of the genuine secondary emission. The presence of high speed reflected electrons could not, of course, be detected by the method of investigation used by the writers.

Since the publication of the authors' experiments on the emission of secondary electrons from platinum, the results of several similar investigations, in addition to that of Farnsworth, have appeared, notably the experiments of Millikan and Barber\* (which Mr. Gill appears to have overlooked), and the more recent investigations of McAllister†. This series of researches, carried out in the Ryerson Physical Laboratory, has led to the conclusion that the maximum velocity of emission of the secondary electrons from copper under electronic bombardment is about 10 volts, and that a potential difference of a few volts is needed between the plate and the grid in order to obtain the saturation value of the current carried by the electrons leaving the plate. Moreover, this latter result is explained by Millikan and Barber as being due to many of the secondary electrons being liberated in "pockets" or holes in the plate, a view similar to that held by the authors.

Mr. Gill's curves are sufficient evidence of the complexity of the factors which need to be taken into consideration in attempting to interpret the results of an investigation of the emission of secondary electrons from a metal surface subjected to electronic bombardment, when an apparatus is used in which there may be a serious interpenetration of the electric fields. The authors make no attempt to discuss Mr. Gill's interpretation of his own results; they only desire to refute the suggestion that the defects which made it impossible for Mr. Gill to draw any useful conclusion with regard to critical voltages from his experiments were, as he assumes, inherent in their own investigation.

\* R. A. Millikan and I. G. Barber, *Proc. Nat. Acad. Sci.* vol. vii, p. 13 (1921); and I. G. Barber, *Phys. Rev.* vol. xvii, p. 322 (1921).

† L. E. McAllister, *Phys. Rev.* vol. xxi, p. 122 (1923).

**XIII. The Relative Intensity of X-Ray Lines.** By FRANK C. HOYT, Ph.D., National Research Fellow\*.

**I. Introduction.**

**T**HE uniform success of Bohr's correspondence principle † as a criterion for the occurrence and state of polarization of spectral lines and as a means of at least qualitative estimation of relative intensities makes it of the greatest importance to attempt its more exact quantitative application. This principle only states the general method by which we are to obtain an estimate of the relative frequency of occurrence of different quantum transitions, but does not lead to an unambiguous expression for the intensity of a given line. Among various plausible expressions, however, we might hope to discriminate by a comparison with experimental values. Kramers ‡ has been able to obtain approximate values for the relative intensities of the fine-structure components of hydrogen and helium lines as well as of the components into which these lines are split up in the presence of electric fields. In this connexion he has suggested how more accurate values may be calculated, but the exact comparison with experiment is not possible for these problems at present, and it may be that the question may be more advantageously attacked in the X-ray region where, except for the increased complexity of the atomic model, the experimental and theoretical problem is in certain respects simpler.

This paper contains a brief discussion of the factors that must be taken into account in a complete theory of the intensity of X-ray lines, and some calculations are made on the basis of the simplest atomic model possible.

**II. Correspondence Principle and Intensity of Spectral Lines.**

The correspondence principle establishes a relation between the quantum theory of radiation and the motion of the particles in the atom, which shows the closest possible analogy with the classical relation between electromagnetic

\* Communicated by Prof. N. Bohr.

† N. Bohr, "On the Quantum Theory of Spectral Lines," *D. Kgl. Danske Vidensk. Selsk. Skifter*, 1, iv.1 (1918). Compare also 'Three Essays on the Theory of Spectra and Atomic Constitution,' Cambr. Univ. Press, 1922.

‡ H. A. Kramers, "Intensities of Spectral Lines," *D. Kgl. Danske Vidensk. Selsk. Skifter*, 8, iii.3 (1919).

radiation and the motion of a system of electrified particles. The principle has been developed by the consideration of systems for which the solution of the mechanical equations of motion can be represented as a superposition of harmonic vibration components\*. This means that the displacement of every particle can be represented as a function of the time  $t$  by a trigonometric series of the type

$$\rho = \sum_{-\infty}^{+\infty} \dots \sum_{-\infty}^{+\infty} C_{\tau_1, \dots, \tau_s} \cos [2\pi(\tau_1\omega_1 + \dots \tau_s\omega_s)t + \delta_{\tau_1, \dots, \tau_s}], \quad (1)$$

where the quantities  $\omega_1, \dots, \omega_s$  are the so-called fundamental frequencies of the motion, while  $\tau_1, \dots, \tau_s$  are integers. Since obviously a similar expression will hold for the component in a given direction of the resultant electric moment of the atom, the radiation which on ordinary electrodynamics would be emitted by the system would at any moment be composed of trains of harmonic waves with frequencies

$$\tau_1\omega_1 + \dots \tau_s\omega_s, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

According to the quantum theory the stationary states are defined by a set of conditions which may be written

$$I_1 = n_1 h, \dots, I_s = n_s h, \quad . \quad . \quad . \quad . \quad (3)$$

where  $n_1, \dots, n_s$  are integers and  $h$  Planck's constant, while  $I_1, \dots, I_s$  are quantities describing certain mechanical properties of the motion. The energy of the system depends on the quantities  $I_1, \dots, I_s$  in such a way that the energy difference  $\delta E$  of two neighbouring mechanical motions is expressed by

$$\delta E = \omega_1 \delta I_1 + \dots \omega_s \delta I_s, \quad . \quad . \quad . \quad . \quad (4)$$

The frequency emitted during a transition between two stationary states for which  $n_1, \dots, n_s$  is equal to  $n'_1, \dots, n'_s$  and  $n''_1, \dots, n''_s$  respectively, is given by the well-known relation

$$\nu = \frac{1}{h} [E(n'_1, \dots, n'_s) - E(n''_1, \dots, n''_s)], \quad . \quad . \quad (5)$$

According to (5) we consequently have

$$\nu = \int_{I''}^{I'} \omega_1 \delta I_1 + \dots \omega_s \delta I_s, \quad . \quad . \quad . \quad . \quad (6)$$

If for the "path of integration" in the  $s$ -dimensional " $I_1, \dots, I_s$  space" we chose a straight line connecting the

\* A brief survey of the principles on which the applications of the quantum theory to atomic problems are based will be found in an article by N. Bohr, *Zs. für Phys.* xiii. p. 113 (1923).

points corresponding to the stationary states, that is, if we put

$$\left. \begin{aligned} I_1 &= h[n_1'' + (n_1' - n_1'')\lambda], \\ I_2 &= h[n_s'' + (n_s' - n_s'')\lambda], \end{aligned} \right\} \dots \dots \dots (7)$$

where  $\lambda$  is a quantity which takes all values from 0 to 1, the expression (6) assumes the simple form

$$\nu = \int_0^1 [(n_1' - n_1'')\omega_1 + \dots (n_s' - n_s'')\omega_s] d\lambda, \quad (8)$$

and states that the frequency of the emitted radiation may be considered as a mean value of the frequency of one of the harmonic components occurring in the motion of the system, represented by (1), if we put

$$\tau_1 = n_1' - n_1'', \dots \tau_s = n_s' - n_s''. \quad (9)$$

The correspondence principle states now that the presence in the electrical moment of the system of the harmonic component of this frequency must be regarded as the cause of the occurrence of the transition considered. Taking the view that the transitions are spontaneous processes\*, this principle leads us to assume that the probability that a certain transition takes place within a given time-interval may be estimated from the amplitude of the corresponding harmonic component by a comparison with the intensity of the radiation to which on classical electrodynamics this harmonic component would give rise. On ordinary electrodynamics the amount of radiation emitted in unit time from an electron performing linear harmonic vibrations with frequency  $\omega$  and amplitude  $C$  is given by

$$\frac{\Delta R}{\Delta t} = (2\pi)^4 \frac{2e^2}{3c^3} C^2 \omega^4; \quad (10)$$

and we may thus hope to effect such a comparison if we estimate the probability of transition by a process of averaging in such a way that, if we write

$$A'_{\nu} h\nu = (2\pi)^4 \frac{2e^2}{3c^3} Q^2 \nu^4 \quad (11)$$

where  $A'_{\nu}$  denotes the probability of transition in unit time,  $Q^2 \nu^4$  can be considered as a kind of mean value of  $C^2 \omega^4$  where  $\omega$  and  $C$  are the frequency and amplitude of the corresponding harmonic component. We know that  $\nu$  may be represented as an average value of the  $\omega$ 's by means of equation (8), but in the present state of the quantum theory

\* Cf. A. Einstein, *Phys. Zeit.* xviii. p. 121 (1917).

we are left to conjectures in regard to the calculation of  $Q$ . However, as Kramers has already suggested, a reasonable procedure would be to take  $Q$  as an average of  $C$  over the same path in the  $I$ -space as may be used for  $\nu$ . Thus we may immediately write down as possibilities

$$Q = \int_0^1 C_\lambda d\lambda \quad . \quad . \quad . \quad . \quad . \quad (12a)$$

and

$$Q^2 = \int_0^1 C_\lambda^2 d\lambda; \quad . \quad . \quad . \quad . \quad . \quad (12b)$$

or, since  $Q$  and  $\nu$  are to be averaged along the same path, we may also write

$$Q\nu^2 = \int_0^1 C_\lambda \omega_\lambda^2 d\lambda \quad . \quad . \quad . \quad . \quad . \quad (12c)$$

and

$$Q^2\nu^4 = \int_0^1 C_\lambda^2 \omega_\lambda^4 d\lambda. \quad . \quad . \quad . \quad . \quad . \quad (12d)$$

Considering our present ignorance of the mechanism of the emission of spectral lines, it seems hardly possible to distinguish between these by *a priori* arguments, and yet the differences between them are not altogether without theoretical significance. Thus (12d) is to be preferred if we wish to average the rate of emission of energy, as given by ordinary electrodynamics, during a slow change from one stationary state to another. In such a case, of course, the radiation would not be monochromatic; and if we wish rather to emphasize the fact that in reality it is, we may make the comparison with a monochromatic oscillator of which the amplitude only is found by an averaging process. We are then led to calculate  $Q$  by (12a) or (12b) and to take  $\nu$  as the actual frequency. We have further to consider Kramers' \* suggestion of a logarithmic method of averaging. In this way we obviate the choice between taking the average of a square or squaring the average of the first power, since both give the same result. Thus we can write also

$$\log Q^2 = \int_0^1 \log C_\lambda^2 d\lambda \quad . \quad . \quad . \quad . \quad . \quad (13a)$$

or

$$\log Q^2\nu^4 = \int_0^1 \log (C_\lambda^2 \omega_\lambda^4) d\lambda. \quad . \quad . \quad . \quad (13b)$$

\* Cf. H. A. Kramers, *loc. cit.*, footnote, p. 46. The general arguments brought forward there against the strict validity of any simple mean value of the type in (12) or (13) cannot be maintained. (Cf. N. Bohr, *Zs. für Physik*, xiii. p. 149 (1923).

We have, then, at least six conceivably possible methods of calculating  $Q^2\nu^4$ . The problems considered by Kramers offered no sufficient basis for a distinction between them by means of comparison with experiment; and it is the purpose of this paper to examine the way in which this may be done by means of measurements on the relative intensity of X-ray lines.

### III. X-ray Spectra and the Correspondence Principle.

According to the quantum-theory picture, the excitation of characteristic X-rays consists in the removal of an electron from one of the inner orbits, and the atom is then ready for emission, which takes place by transition of an electron from another orbit to fill the place left vacant. The intensity of the radiation emitted depends on the relative probability or frequency of occurrence of this transition as compared with other possible ones. Denoting, as above, the probability that a spontaneous transition from a state ('') to a state (') takes place within a time-interval  $\Delta t$ , by  $A'_{''}\Delta t$  we get for the total amount of radiation  $R$  emitted in unit time as a consequence of a transition of this type

$$R = N' A'_{''} h\nu,$$

where  $N'$  is the mean number of atoms present at any moment in the state ('). From this expression it follows, in the first place, that the relative intensity of the X-ray lines which correspond to the various transitions which may occur after the removal of the same electron in the atom, and which have the same critical potential of excitation, are independent of the conditions under which the lines are produced\*; and this conclusion is confirmed by the experiments of Webster† and Wooten‡.

The theoretical estimation, by the correspondence principle, of the relative intensities of such lines requires of course a definite picture of atomic constitution. The general outlines of such a picture are furnished by Bohr's § recent theory, in which the nature and arrangement of the electron orbits is consistent not only with the general character of the spectra

\* Cf. S. Rosseland, *Phil. Mag.* lxx. p. 65 (1923).

† Cf. Webster, *Phys. Review*, vii. p. 599 (1916); ix. p. 220 (1917).

‡ Cf. Wooten, *Phys. Review*, xiii. p. 71 (1919).

§ N. Bohr, *Fysisk Tidsskrift*, xix. p. 153 (1921); in German translation, *Zs. für Phys.* ix. p. 1 (1922); in English translation, 3rd essay in the volume cited on p. 135, note.



of the elements, but also with the periodicity of their physical and chemical properties. The classification of the electron orbits in this theory is based on the assumption that the motion of each individual electron in the atom to a first approximation may be described as a plane periodic orbit, on which is superposed a uniform rotation in its plane. Thus each orbit is represented by a symbol  $n_k$ , where the "principal" quantum integer  $n$  is analogous to the quantum number which defines the stationary states of a periodic Keplerian motion, while the subordinate quantum number  $k$  corresponds to the azimuthal quantum integer appearing in Sommerfeld's theory for the fine-structure of the hydrogen lines. The radial quantum integer appearing in the latter theory is in our notation equal to  $n-k$ . For electron orbits well in the interior of the heavier atoms, the dimensions differ but little from those of orbits with the same quantum number described by an electron revolving about the nucleus in the absence of other electrons. For the outer parts of the atom, however, the form and dimensions of the orbits will differ considerably from those of such orbits, since here the effect of repulsion from the other electrons is no longer small compared with the attraction towards the nucleus.

The principal quantum integer determines to a first approximation the energy of the orbit, and we thus have a natural division into groups of orbits with the same value of  $n$  but different values of  $k$ . These groups correspond to the K, L, M, ... "levels" in X-ray spectra, and their further divisions into sub-groups is consistent with the classification of the X-ray energy levels worked out by Coster\* and Wentzel†. The interpretation of these levels, and in particular their characteristic changes with atomic number, have been more fully discussed in their relation to this theory in a recent paper by Bohr and Coster‡. It has also been possible to establish certain simple empirical combination rules which suggest the way in which the correspondence principle is to be applied here. In fact, it appears from the work of the last-named authors that we may distinguish from among the others certain so-called "regular" levels, which are purely of the  $n_k$  type. The number of these levels corresponds exactly to the number of sub-groups of electron orbits required by the theory, and the empirical rules for the

\* Phil. Mag. xliii. p. 1070, xliv. p. 546 (1922).

† Zs. für Phys. vi. p. 84 (1921).

‡ Zs. für Phys. xii. p. 342 (1923).

occurrence of transitions between them are such as would be predicted by the application of the correspondence principle to central motion. The remaining levels may be called "irregular"; and although their detailed interpretation is still doubtful, a preliminary designation by means of two  $k$  numbers has been employed, because presumably they are closely connected with the interaction of *two* sub-groups resulting from the removal of an electron from one of them.

This representation of the X-ray levels in relation to the structure of electron orbits provides us with a basis for the quantitative application of the correspondence principle. In the case of transitions between regular levels, it seems not unreasonable to suppose that we can estimate the intensities by direct comparison with central orbits. In general it is not at present possible to determine exactly the motion in the electron orbits, but for those well in the interior of the atom the motion will be approximately Keplerian. Thus for the energy levels corresponding to the removal of an electron from one of these inner orbits we may make use of the work of Kramers on the fine-structure intensity of hydrogen and helium lines. We will, in the first instance, make our calculations as though the nuclear charge were constant, and as though we had to do with the probability of transition of only one electron. We can then consider how these results may be modified to take account of the fact that the effective nuclear charge is different for the different orbits, and that in a sub-group we have really several orbits with the same values of  $n$  and  $k$ .

#### IV. Calculations and Results.

For central motion of a single electron about the nucleus, the expression corresponding to (1) for the displacement in any direction must take the form \*

$$\xi = \sum_{-\infty}^{+\infty} C_r \cos 2\pi(\tau\omega + \sigma)t. \quad . \quad . \quad . \quad (14)$$

Here  $\omega$  and  $\sigma$  are the frequencies of oscillation of  $r$  and  $\phi$  respectively. The amplitude coefficients depend only on  $\tau$ ,

\* Cf. N. Bohr, *D. Kgl. Danske Vidensk. Selsk. Skrifter*, 8, iv. (1918), part i. p. 33. Cf. also E. P. Adams, "The Quantum Theory," Bull. Nat. Research Council, vol. i. part 5, p. 367.

and Kramers has shown that for the relativity ellipses we have\*

$$C_{\tau} = -\chi^2 \frac{1}{2\tau} [(1 + \epsilon') J_{\tau-1}(\tau\epsilon) - (1 - \epsilon') J_{\tau+1}(\tau\epsilon)], \quad (15)$$

where

$$\begin{aligned} \chi &= \frac{1}{4\pi^2 N e^2 m}, & I &= n h, \\ \epsilon' &= \frac{P}{I}, & P &= k h, \\ \epsilon &= \sqrt{1 - \epsilon'^2}. \end{aligned}$$

Here  $n$  and  $k$  are the principal and subordinate quantum integers, and  $N$  is the atomic number.  $J_{\tau-1}$  and  $J_{\tau+1}$  are Bessel functions of the order indicated by the subscript.

To calculate the value of  $Q^2\nu^4$  by any one of the methods suggested in the expressions in (12) and (13), we must first express the  $C_{\tau}$  and  $\omega$  for any transition for which  $n' - n'' = \pm \tau$  and  $k' - k'' = \pm 1$  as a function of  $\lambda$  by means of the relations

$$\begin{aligned} I &= h[n'' + (n' - n'')\lambda], \\ P &= h[k' \pm \lambda], \end{aligned}$$

corresponding to (7). It will, in general, be impossible to evaluate directly the integrals thus obtained, but by graphing  $C$  as a function of  $\lambda$  and measuring the area under the curve, sufficiently accurate values may be obtained. In the case of the logarithmic integral (13a), which becomes infinite for  $\lambda=0$  for certain transitions, an approximate expression for small values of  $\lambda$  was used which could be integrated directly. The quantity  $\omega$  which occurs in (12a) and (12b) is approximately the frequency of revolution in the orbit, and may be readily calculated as a function of  $\lambda$ . For the other methods of estimating  $Q^2\nu^4$ , measured values of  $\nu$  can be used.

The values of  $Q^2\nu^4$  have been calculated in this way, assuming the nuclear charge in (15) constant, for the transitions between regular levels that may take place after the removal of an electron from a  $1_1$  orbit—that is, for the K-series transitions. For these lines the relative intensity will be given by the relative values of  $Q^2\nu^4$ , as seen from (11), in so far as we have to do only with the probability of transition of a single electron. But, as already mentioned, we have, for each line, to consider the probability of transition to a  $1_1$  orbit from a number of orbits with the same values of  $n$  and  $k$ . It is then easily seen that we must multiply our value of  $Q^2\nu^4$  by the number of electrons in the sub-group  $n_k$  to which the initial orbit belongs, which may be denoted by  $r$ .

\* H. A. Kramers, *loc. cit.* p. 298.

Relative Intensities of the K-Series Transitions of Rhodium.

$$\nu_{\alpha_1}^4 : \nu_{\beta_1}^4 : \nu_{\beta_2}^4 = 1 : 1.587 : 1.724.$$

Relative Values of  $Q^2\nu^4r$ .

Transition.	1. $Q^2\nu^4 = \nu^4 \int_0^1 C_{\lambda^2} d\lambda.$	2. $Q\nu^2 = \nu^2 \int_0^1 C_{\lambda} d\lambda.$	3. $\log Q = \int_0^1 \log C_{\lambda} d\lambda.$	4. $Q^2\nu^4 = \int_0^1 C_{\lambda}^2 \omega_{\lambda}^4 d\lambda.$	5. $Q\nu^2 = \int_0^1 C_{\lambda} \omega_{\lambda}^2 d\lambda.$	6. $\log Q^2\nu^4 = \int_0^1 \log C_{\lambda}^2 \omega_{\lambda}^4 d\lambda.$	Experiment.
$\alpha_1 2s \rightarrow 1_1 \dots$	1	1	1	1	1	1	1
$\beta_1 3s \rightarrow 1_1 \dots$	.458	.409	.293	.28	.21	.126	.29
$\beta_2 4s \rightarrow 1_1 \dots$	.332	.262	.105	.10	.075	.0075	.05

The relative intensities of the K-series lines thus computed in six different ways are given in the table. The values of  $\nu^4$  used are the empirical values for rhodium, and the number of electrons in the sub-groups is assumed to be that given by Bohr's theory for this element—i. e., 4 in the  $2_2$  group, 6 in the  $3_2$ , and 6 in the  $4_2$  \*. For other regular transitions than those leading to  $\alpha_1$ ,  $\beta_1$ , and  $\beta_2$  there is no corresponding amplitude in the motion because  $k' - k'' = \pm 1$ . The experimental values for rhodium as estimated from Webster's and Wooten's results are also included. Webster's values are for rhodium only, and uncorrected for absorption in the glass of the X-ray tube, while those of Wooten are for molybdenum and palladium, corrected for absorption, but with  $\alpha_1$  and  $\alpha_2$  unseparated. By combining the two we may get a value for  $\beta_1$  which is probably correct to within 2 or 3 per cent. In the case of  $\beta_2$  the value can hardly be regarded as much more than an estimation of the order of magnitude. It is unfortunate that there are no experimental values for other elements.

As to the lines of the K-series that involve irregular levels, it should be noted that the only one of appreciable intensity is  $\alpha_2$ , which is about  $\frac{3}{4}$  as strong as  $\alpha_1$ . The line  $\beta_3$ , which is of this class, is very weak, and the corresponding companion of  $\beta_2$  has not yet been observed. Lines corresponding to other transitions have not been found.

As before mentioned, the nuclear charge has been assumed constant, and hence does not affect the calculated relative values. We are able, of course, to calculate the effective nuclear charge in the stationary states, but we do not know how to represent it as a function of  $\lambda$  for purposes of averaging. But since the amplitude coefficients are inversely proportional to the effective nuclear charge, we see that the general effect will be to increase the values for  $\beta_1$  and  $\beta_2$ . We may, however, make a very rough estimate of the order of magnitude from the empirical screening constants. In the case of the averages as taken in columns 1 and 2 of the table, the effect may be as high as 30 per cent. for  $\beta_1$  and 100 per cent. for  $\beta_2$ . For the logarithmic average and the last two in which  $\omega$  is within the integral sign, the effect

\* It is to be noted, however, that according to Bohr's theory of atomic structure, the  $4_2$  orbit in rhodium belongs to a sub-group which is still in a state of development. Thus for the heaviest elements there are 8  $4_2$  orbits, and for some of the lighter ones there are only 4. This implies corresponding changes in the intensity of  $\beta_2$  which are much larger than those due to changes in the relative values of  $\nu^4$ . Similar characteristic changes with atomic number are to be expected for other lines, and their examination would furnish an interesting test of the theory.

will be considerably smaller, because the way in which the amplitude changes with  $\lambda$  is such as to emphasize the values where  $\lambda$  is small and the correction nearly negligible. Here the effect is probably from 5 to 10 per cent. in the case of  $\beta_1$  and 30 to 50 per cent. in the case of  $\beta_2$ , which latter is comparable with the experimental error. The corrections will, of course, be still smaller for elements of higher atomic number, but for these we lack any empirical values.

For the lines of the L- and M-series the rather lengthy computations of the average amplitudes have only been made in a few cases, as the uncertainties due to changes in the nuclear charge are greater, and there are no empirical values for comparison. However, it appears that here also the values will be of the right order of magnitude so far as can be seen from estimation of intensities from photographic plates. It is much to be hoped that in the future we may have some experimental values for L-series lines that are free from errors due to absorption in the glass of the X-ray tube.

### V. Conclusions.

It would seem safe to conclude from the comparison with empirical values that it is possible by means of averages between the stationary states of the type employed to obtain a satisfactory representation of the intensities of X-ray transitions between regular energy levels. As to distinguishing between the different averages, we may only say with some certainty that those in columns 1, 2, and 6 may be discarded as differing too widely from the empirical values. Between the other three we cannot distinguish very sharply, although, strictly speaking, the best agreement is for the results in column 3, where the intensity is calculated by comparison with a monochromatic oscillator, the amplitude of which is found by a logarithmic average. It will be well, however, to reserve judgment on this point until we have data on the heavy elements.

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**XIV. Poisson's and Green's Theorems in Riemann's  $n$ -manifold both when it is space-like and when time-space-like. By Prof. ALEX. MCAULAY, M.A., University of Tasmania\*.**

**T**HE notations of this paper had been used in two other papers sent to the Phil. Mag. a little earlier than the present paper and were not again explained. As, however, these two papers have never appeared, it may now be said (May 1923) that the notations will be found in "Multenions and Differential Invariants," I., II., III. (Proc. Roy. Soc., A. vol. xcix. p. 292, vol. cii. p. 210, and some vol. still unknown).

§ 1. *Scope of the paper and enunciation of the two principal theorems.*—In this § 1 Poisson's theorem is enunciated for each of the two species of Riemann's  $n$ -manifold. In § 2 a minute explanation of the meaning of the enunciations is given. The opportunity is used to present several aspects of matters affecting the theorems, which are at the same time of general import. The proof follows in § 3, and the paper concludes with a treatment of Green's theorem for the case of the  $n$ -manifold.

In a space-like manifold—that is, one all of whose  $n$ -dimensions are real—Poisson's theorem becomes

$$\left. \begin{aligned} V_0 \nabla (\bar{\eta} \nabla \int^n \int h \bar{m} db) &= \pi_n \bar{m}, \\ \text{where } h &= (\text{distance})^{2-n}/(n-2), \end{aligned} \right\} \dots \dots (1)$$

except when  $n=2$ , in which case  $h = \log (\text{distance})$ .

In a time-space-like manifold—that is, a manifold of which one dimension is time-like or imaginary and the remaining  $n-1$  are space-like or real—the theorem becomes

$$\left. \begin{aligned} V_0 \nabla (\bar{\eta} \nabla \int^{n-1} \int h m V_0 d\alpha) &= \pi_{n-1} \bar{m}, \\ \text{where } h &= (2z + V_0^2 \iota \nabla z)^{\frac{3-n}{2}} / (n-3), \quad z = \frac{1}{2} (\text{distance})^2, \end{aligned} \right\} \dots (2)$$

except when  $n=3$ , in which case

$$(n=3), \quad h = \frac{1}{2} \log (2z + V_0^2 \iota \nabla z). \dots \dots (3)$$

It may be stated also that, putting

$$\nu = N \nabla z = V_1 \iota V_2 \eta \iota \nabla z, \dots \dots (4)$$

$h$  may alternatively be defined by

$$h = (-V_0 \nu \eta^{-1} \nu)^{\frac{3-n}{2}} / (n-3), \dots \dots (5)$$

except when  $n=3$  as before.

\* Communicated by the Author.

It must be explained that

$$\pi_2 = 2\pi, \quad \pi_3 = 4\pi, \quad \pi_4 = 2\pi^2,$$

and generally  $\pi_n$  is the solid angle subtended at a point by the whole of an  $n$ -manifold when the manifold is space-like. [The similar solid angle in a time-space-like manifold, but subtended by the whole of the manifold within either light semi-cone, or subtended by the whole without the cone, is in both cases infinite.] If  $k$  is any positive integer, the following are the values of  $\pi_n$  [except for  $\pi_2$ , though the formula is easily modified to cover the case by writing  $2^{k-1}(k-1)!$  for the denominator on the right of the first of the following equations]:

$$\begin{aligned} \pi_{2k} &= (2\pi)^k / [2 \cdot 4 \dots (2k-2)], \\ \pi_{2k+1} &= 2(2\pi)^k / [1 \cdot 3 \dots (2k-1)]. \end{aligned} \quad (6)$$

Here is a table for  $\pi_n$ , calculated by 5-figure logarithms, so that last-figure accuracy is not guaranteed:—

$n$ .	$\pi_n$ .	$n$ .	$\pi_n$ .	$n$ .	$\pi_n$ .	$n$ .	$\pi_n$ .
2	6.2832	8	32.470	14	8.3898	20	.51614
3	12.566	9	29.687	15	5.7217	21	.29294
4	19.739	10	25.502	16	3.7653	22	.16215
5	26.319	11	20.725	17	2.3967	23	.08765
6	31.006	12	16.023	18	1.4786	24	.04631
7	33.074	13	11.838	19	.88582	25	.02394

$\pi_n$  rapidly diminishes beyond the limits of the table;  $\pi_{100} = 10^{-38} 2.3683$ . Note that a maximum of about 33 is reached at  $n=7$ .

$\pi_n$  is defined as the area of a small sphere, radius  $r$ , in an  $n$ -dimensional space, divided by  $r^{n-1}$ . Thus the area and volume of the sphere are  $\pi_n r^{n-1}$  and  $\pi_n r^n/n$  respectively, and the circumference and area of a circle of the same radius in the same space are  $\pi_{n-1} r^{n-2}$  and  $\pi_{n-1} r^{n-1}/(n-1)$  respectively. The volume of the sphere is generated by the motion of a circle of varying radius, which moves parallel to itself and whose radius is  $r \cos \theta$  when it is at a distance  $r \sin \theta$  from the centre of the sphere. Hence we have

$$\pi_n/n = (\pi_{n-1}/(n-1)) \cdot 2 \int_0^{\frac{1}{2}\pi} (\cos \theta)^n d\theta.$$

From this we further deduce that

$$\pi_{n+2}/\pi_n = 2\pi/n,$$

and (6) then readily follows.

§ 2. The meaning of the theorems explained.—Take  $\rho$  for



position vector, and  $\eta$  for the fundamental covariant vector linearity, so that the scalar form is  $V_0 d\rho \eta d\rho$  (though in a space-like manifold, except when consistency forbids, it is better to reverse the sign of  $\eta$ ). Whenever a bar, as with  $\bar{\eta}$  and  $\bar{m}$  in (1) and (2) of § 1, is placed over a symbol it is understood that the symbol is an invariant, covariant, or contravariant quantity multiplied by  $k$ , where  $k = |\eta|^{1/2}$  and  $|\eta|$  stands for the determinant of  $\eta$ . Such a barred symbol is called a density. [Will somebody invent a better word?—this clashes confusingly with density as applied to matter.] Thus  $\bar{\eta}$  is defined to mean the frequently recurring linearity  $k\eta^{-1}$ .  $\bar{m}$  is  $k$  multiplied by a scalar invariant function of position; it appears as the analogue below of material density when Poisson's theorem is taken in its strictly original sense.

(1), so obviously like the original Poisson theorem, serves to introduce (2). Let, in the case of (1),  $r (=T\rho)$  be the distance of the point  $\rho$  from the origin  $O$ , whether of three-dimensional Euclidean space or of  $n$ -dimensional Riemannian. In the three-dimensional case, if we put  $h = r^{-1}$  [see (1)] and form the volume integral  $\iiint h \bar{m} db$  for any given volume, including the origin, Poisson's equation asserts that

$$4\pi \bar{m} = \nabla^2 \iiint h \bar{m} db = S \nabla (\nabla \iiint h \bar{m} db),$$

the  $\bar{m}$  on the left meaning the value at the origin. In the general Riemannian case  $h$  becomes  $r^{2-n}/(n-2)$ , where, when we are using equiradial coordinates,  $r$  may still be defined as  $T\rho$ , but in general must be defined as distance (along a geodesic) between the element  $db$  and the origin. The operator  $\nabla^2 = S \nabla \nabla$  becomes the invariant operator

$$V_0 \nabla (\bar{\eta} \nabla [ \ ])$$

(not that the result is an invariant, but that it is an invariant density), which for the future we shall write as  $V^2 \bar{\eta} \nabla$ . The  $4\pi$  becomes  $\pi_n$ , and the equation becomes

$$V_0 \nabla \bar{\eta} \nabla \int^n \int h \bar{m} db = \pi_n \bar{m}.$$

For the value of a quantity at the origin, or more generally at the point belonging to the operator *outside the integral*, we shall use the suffix  $O$  whenever for clearness it seems desirable. The other end of the distance defining  $h$  is the point belonging to the element  $db$  *inside the integral*. Such a point we will denote when it seems desirable by  $I$ , and a function at  $I$  by the suffix  $I$ . Thus in the present

case, putting in  $O$  and  $I$  everywhere,

$$\begin{aligned} & V_O \nabla_O \bar{\eta}_O \nabla_O \int^n \int h_{OI} \bar{m}_I db_I = \pi_n \bar{m}_O, \\ \text{or} \quad & V_O (\nabla \bar{\eta} \nabla)_O \int^n \int h m_I db_I = \pi_n \bar{m}_O. \end{aligned}$$

Even when we pass one or both of the symbols  $\nabla$ , or the symbol  $\bar{\eta}$  from outside to inside, we can retain the suffix  $O$  to remind us that the symbol still *belongs* to the point  $O$ , though it has temporarily migrated to a neighbour's location.

These fairly familiar matters have been detailed by way of introduction. Let me now try to indicate what I finally succeeded in satisfying myself of, in connexion with a time-space-like manifold. I started with the full expectation that, whether I could find it or not, there was some theorem very analogous to (1), and like (1) referring to an  $n$ -dimensional region, and treating all geodesics impartially. *There is no such theorem.* Poisson's original theorem is interpretable in connexion with sources whose discharge takes place uniformly in all directions along geodesics. Now the solid angle (infinite) of all the three compartments (the inside of two semi-cones, past and future, and the spatial outside) into which the light-cone of a point partitions the manifold is in each case infinitely nearly concentrated on the cone. Hence, strengths of source being finite, the discharges when uniform in all directions, as prescribed, must be solely along the rays (*corresponding* to geodesics) of the cone. *But* there is nothing given by the fundamental form  $V_0 d\rho \eta d\rho$  which enables us to divide the rays up into equal bundles: we cannot do so even in a Galilean manifold. The very conception of such a partition of the rays requires us to assign a time axis; it cannot be effected absolutely. This is our first great leading; we must suppose a congruence of time-like curves filling the manifold to be given, in order to fix the time axis everywhere—that is, if we would talk about sources discharging uniformly in all directions along geodesics (or their limiting rays on the cone). Proceeding to the details of the discharge so postulated, we naturally discover that the underlying phenomenon is  $(n-1)$ -dimensional, instead of  $n$ -dimensional. It is a phenomenon referring to an unbounded prescribed space-like surface (giving an  $(n-1)$ -dimensional *space*), at every point of which there is a prescribed contravariant time-like vector which may be regarded as specifying the *time* axis at that point.

The last sentence truly describes the mathematical requirements for the application of (2); a given wholly



well as by  $h$ . It is this element  $V_0 \iota d\alpha$  of tubular cross-section, not the corresponding portion of the region, which is analogous to the element of volume in Poisson's original theorem; for  $\bar{m}$  occurs outside the integral as well as inside, and  $h$  is the distance function connecting points  $O$  with points  $I$ . What still remains under the integral sign, namely  $V_0 \iota d\alpha$ , is analogous to what similarly remains in Poisson's case, the element of volume. This remark will be found true in physics generally. It is always the three-dimensional cross-section of a physical four-dimensional tube, whose generators are time-like curves, which is the mathematical representative of the physicist's three-dimensional volume. There seems no exception; certainly there is not in the domains of matter and electricity. [See my third R.S. paper on "Multenions and Differential Invariants." This paper was despatched many months before the meeting of the British Association last year (meaning the year 1921): I read that the tubes received some attention at that meeting.] It appears from the present paper that this dominance of the  $n$ -dimensional tubes is a mathematical consequence of the fundamental properties implied by  $\eta$ ; it is not, on the contrary, something in addition imposed by an anthropomorphic legislator of Nature: the legislator has merely said, Let the world be Riemannian and for the rest you may do as you please.

The diagram implies correctly that  $da$  is a (scalar) component of the (vector)  $d\alpha$  and that  $\nu$  is a (vector) component of the (vector)  $\nabla z$ , but is misleading as to the relative magnitudes of original and component of original. Thus actually

$$\begin{array}{ccc} \text{magnitude of } da & > & \text{magnitude of } d\alpha, \\ \text{,,} & \nu > & \text{,,} \quad \nabla z. \end{array}$$

The reader is warned to beware of misdirection from surprises of this kind, which, of course, are due to the imaginary dimension coming into comparison with the real dimensions.

As the diagram implies, it is often desirable to consider an  $n$ -dimensional region  $\int (db)$  as bounded by two faces, that is, two members  $\int (d\alpha)$  of the family, and by an edge consisting of generators  $\int (\iota ds)$  of the tubes,  $ds$  being interval measured along  $\iota$ . [ $db, d\alpha, d\alpha_B, ds_2$  are all cases of  $ds_a$ , and are therefore all anti-density covariant multenions;  $db$  being a scalar,  $d\alpha$  a vector, and  $ds_2$  a  ${}_nV_2$ ].  $ds_2$  is a common element of boundary of  $\int (d\alpha)$  and  $\int (d\alpha_B)$ .  $d\alpha_B$  may be taken as a parallelogram-like element of which  $n-2$  sides belong to

$d\varsigma_2$  and the remaining one is  $\iota ds$ . It is convenient to introduce a vector  $d\sigma$  parallel to  $d\alpha_B$ , but of the one dimension due to  $ds$  less than  $d\alpha_B$ . Thus

$$\left. \begin{aligned} d\alpha_B &= V_1 \iota d\varsigma_2 \cdot ds = d\sigma \cdot ds, \\ d\sigma &= V_1 \iota d\varsigma_2, \\ V_3 d\varsigma_2 d\sigma &= 0 = V_3 d\varsigma_2 d\alpha_B = V_3 d\varsigma_2 d\alpha. \end{aligned} \right\} \dots (7)$$

[Note that between two consecutive members  $\int(d\alpha)$  the  $ds$  may or may not vary from tube to tube,  $\iota$ , according to our prescription in the problem in hand.]  $d\sigma$  is to be taken as the vector element of boundary of  $\int(d\alpha)$  when we explicitly use  $da(V_0 \iota d\alpha)$  as the element of integration of  $\int(d\alpha)$ .  $da$  is the element of physical volume of the  $(n-1)$ -dimensional physical space  $\int(d\alpha)$  and  $d\sigma$  is the corresponding element of physical boundary;  $d\sigma$  is *not* in the region  $\int(d\alpha)$ , but instead it is normal to the tube  $\iota$ .

Our original integration theorem ["Multenions and Differential Invariants," first paper, § 8, eq. (6); there are many misprints in the paper;  $db$  is omitted from the right of the equation here quoted] gives

$$\int^{n-1} \int \phi d\alpha = \int^n \int \phi_9 \nabla_9 db, \dots (9)$$

but in our present notation  $d\alpha$  refers only to the faces, and the present form of (9) will be

$$\int^{n-1} \int \phi d\alpha_B = - \int^{n-1} \int \phi d\alpha + \int^n \int \phi_9 \nabla_9 db. \dots (10)$$

If on bringing the two faces close together, and prescribing that  $ds$  is common to all the elements of tubes between the faces (this prescribes the consecutive member  $\int(d\alpha)$ , when a particular one is given) we should have  $db = V_0 \iota d\alpha \cdot ds$ . If we could assume the two opposite ends of a tube to cause the sum  $\phi d\alpha + \phi d\alpha'$  to be zero, we should have from (10)

$$(\text{incomplete}) \quad \int^{n-2} \int \phi d\sigma = \int^{n-1} \int \phi_9 \nabla_9 da, \dots (11)$$

exactly similar to (9). Unfortunately for simplicity, this is legitimate only in very special cases.

The true form of (11) may be obtained from our general theorem of integration, by which in particular

$$\int^{n-1} \int \psi d\varsigma_2 = \int^{n-1} \int \psi_9 V_2 d\alpha \nabla_9. \dots (12)$$

Now, by (7)  $d\sigma = V_1 \iota d\varsigma_2$ . Hence by (12)

$$\int^{n-2} \int \phi d\sigma = \int^{n-1} \int \phi_9 V_1 \iota_9 V_2 d\alpha \nabla_9. \dots (13)$$

It will be seen from this, since  $da = V_0 \iota d\alpha$ , that

$$\int^{n-2} \phi d\sigma - \int^{n-1} \phi_0 \nabla_0 da$$

instead of being zero, as stated in (11), consists of two terms,

$$- \int^{n-1} \phi_0 d\alpha V_0 \iota \nabla_0 - \int^{n-1} \phi V_1 (V_2 d\alpha \nabla \cdot \iota),$$

the first involving the derivative  $-V_0 \iota \nabla \cdot \phi$  of  $\phi$  along the tube  $\iota$ , and the second the derivatives of  $\iota$  in the form  $-V_1 (V_2 d\alpha \nabla \cdot \iota)$ . This last has a simple geometrical interpretation. Integrating it over a finite portion of  $\int (d\alpha)$ , we have by (12)

$$- \int^{n-1} \phi V_1 (V_2 d\alpha \nabla \cdot \iota) = - \int^{n-2} \phi V_1 d\sigma_2 \iota = \int^{n-2} \phi d\sigma$$

by (7). This geometrical result reminds us of the important fact that  $\int^{n-2} \phi d\sigma$ , for a closed boundary, in general differs from zero. In a Euclidean space it would be zero.

Of special importance is the following particular case of (13) obtained by putting  $\phi(\cdot) = V_0 \bar{\tau}(\cdot)$ , where  $\bar{\tau}$  is a contravariant vector density:

$$\int^{n-2} \phi V_0 \bar{\tau} d\sigma = \int^{n-1} V_0 d\alpha V_1 \nabla V_2 \bar{\tau} \iota. \quad (14)$$

§ 3. *Proof of the two forms of Poisson's theorem.*—Let the position vector  $\rho$  of a point be given by

$$\rho = \sum_{c=1}^n x_c \iota_c, \quad \left. \vphantom{\sum_{c=1}^n} \right\}, \quad (15)$$

where  $1 = -\iota_1^2 = -\iota_2^2 = \dots = -\iota_{n-1}^2 = \pm \iota_n^2$ , the upper or lower sign of  $\iota_n^2$  being taken according as the manifold is space-like or time-space-like.

To prove (1) take the point O as origin and use equiradial coordinates ["equiradial" seems a suitable term for the coordinates used in "A new Identity affecting Relativity," etc., Phil. Mag. †]. An asterisk attached to an equation signifies that it is true when the coordinates are equiradial, and in particular when they are Galilean. Thus

$$\left. \begin{aligned} h &= (-\rho^2)^{\frac{2-n}{2}} / (n-2), \\ \nabla h &= -(-\rho^2)^{-\frac{n}{2}} \rho, \\ \nabla^2 h &= 0, \end{aligned} \right\} [h \text{ given by (1)}]. \quad (16)^*$$

except for the point O itself. Draw a small sphere around the origin and consider its boundary as part of the integral boundary. With the origin thus excluded

$$\begin{aligned} 0 &= \nabla^2 \int^n h db = \int^n \nabla^2 h db, \\ &= \int^{n-1} V_0 d\alpha \nabla h. \end{aligned}$$

† [To appear shortly.]

[It is easy to see that  $V_0 d\alpha \nabla h$  is the solid angle subtended by  $d\alpha$  at O.] This result shows that the integral over an arbitrary boundary surrounding the origin is equal and opposite to that of the small sphere; or if both are taken in the same direction radially, they are equal. Now the value for the small sphere is  $\pi_n$ . The well-known argument of three dimensions holds, and we have that with the coordinates chosen

$$\nabla^2 \int^n h \bar{m} db = \pi_n \bar{m}. \quad . \quad . \quad . \quad (17)^*$$

This is the same as (1) in equiradial coordinates and the integral of (1) is an invariant. Hence (1) is true universally.

Similarly for (2). In the present case put  $x_n = t$ , and  $\sum_{c=1}^{n-1} x_c \iota_c$ , and remember that

$$\nabla = \sum_{c=1}^{n-1} \iota_c D_{x_c} - \iota_n D_t. \quad . \quad . \quad . \quad (18)$$

Take O for the origin and use equiradial coordinates with axes so chosen that at the origin  $\iota = \iota_n$ . Thus

$$\left. \begin{aligned} 2z &= \sum x^2 - t^2, \quad \nabla z = \rho, \quad -V_0 \iota \nabla z = t, \\ h &= (\sum x^2)^{\frac{3-n}{2}} / (n-3). \end{aligned} \right\} \quad . \quad . \quad (19)^*$$

This is exactly the same form of  $h$  as we had in the proof of (1), except that here we have  $n-1$ , where before we had  $n$ . Hence

$$[h \text{ given by (2) and (5)}] \quad \nabla^2 h = 0, \quad . \quad . \quad . \quad (20)^*$$

except where  $h$  is infinite, that is, on the axis of  $t$ . [As a matter of fact, our surface  $\int (d\alpha)$ , being space-like, cannot bend round and intersect the axis in a point other than O, so that O is the only singular point.]

We now have

$$\nabla^2 \int^{n-1} h \bar{m} V_0 \iota d\alpha = 4\pi \bar{m}, \quad . \quad . \quad . \quad (21)^*$$

because, first from (20), we may neglect all parts of the integral except near the origin, and there we may put  $\iota = \iota_n$ . The matter has now been reduced exactly to the former case, except that  $x_1, x_2, \dots, x_{n-1}$  replace the former  $x_1, x_2, \dots, x_{n-1}, x_n$ . Hence (2) is true.

At this stage the following remarks seem desirable:—

(1) If the family and congruence have not been prescribed the family may be taken as the planes  $x_n = \text{const.}$  in any given system of coordinates; that is, we may identify our present coordinate  $t$  with our former parameter  $t$ . At the same time we may take  $\iota$  parallel everywhere to  $\iota_n$ , which simplifies the differentiations when we transform (2), say by integration by parts. Instead, we might take  $\eta$  parallel

everywhere to  $\epsilon_n$ . This would make the tubes everywhere orthogonal to the surfaces.

(2) The converse of (1) in all particulars holds. If both family and congruence have been prescribed, we can choose coordinates (flatten the surfaces and straighten the tubes), such that the family again becomes  $x_n = \text{const.}$  and  $\epsilon$  is everywhere parallel to  $\epsilon_n$ ; or instead, if only the family had been prescribed, we could have taken the tubes orthogonal to them, so making  $\eta$  parallel everywhere to  $\epsilon_n$ .

(3) When the family and tubes are already prescribed, we can make  $\epsilon = \epsilon_n$  everywhere, and one particular member of the family become  $x_n = 0$ . Of course, if that one member alone has been prescribed, we can now further take the whole family to be  $x_n = \text{const.}$

We will conclude by proving Green's theorem. Let  $y$  and  $z$  be invariant functions of position. [When we require the original  $z$  of (2), (3), (4), we may use  $Z = \frac{1}{2} (\text{distance})^2$ .] In the space-like manifold integrate twice by parts, the following :

$$\begin{aligned} \int^n \int y V_0 \nabla \eta \nabla z db &= \int^{n-1} \int y V_0 d\alpha \bar{\eta} \nabla z - \int^n \int V_0 \nabla y \bar{\eta} \nabla z db \\ &= \int^{n-1} \int V_0 d\alpha \bar{\eta} (y \nabla z - z \nabla y) + \int^n \int z V_0 \nabla \bar{\eta} \nabla y db. \end{aligned}$$

Here we might have said instead : express

$$\int^{n-1} \int V_0 d\alpha \bar{\eta} (y \nabla z - z \nabla y)$$

as a volume integral. Each of these processes can be imitated in the time-space-like manifold. Perhaps the second is easier to follow. Using (14) express

$$\int^{n-2} \int V_0 d\sigma \bar{\eta} (y \nabla z - z \nabla y)$$

as an  $\int^{(n-1)} \int (d\alpha)$ . Thus we obtain the two forms of Green's theorem, both forms applying to both species of  $n$ -manifold,

$$\left. \begin{aligned} \int^n \int (y V_0 \nabla \bar{\eta} \nabla z - z V_0 \nabla \bar{\eta} \nabla y) db \\ &= \int^{n-1} \int V_0 d\alpha \bar{\eta} (y \nabla z - z \nabla y), \\ \int^n \int V_0 d\alpha (-y V_1 \nabla V_2 \bar{\eta} \nabla z + z V_1 \nabla V_2 \bar{\eta} \nabla y \\ &\quad - \bar{\eta} V_1 V_2 \nabla y \nabla z) \\ &= \int^{n-2} \int V_0 d\sigma \bar{\eta} (y \nabla z - z \nabla y). \end{aligned} \right\} \quad (22)$$

The three dimensional form of (22) used to be known as Green's theorem. Jeans ('Electricity and Magnetism,' § 181) seems to say that Green's theorem, properly speaking, is what (9) and (14) become when we put

$$\phi = V_0 ( ) \bar{\tau},$$

where  $\bar{\tau}$  is a contravariant vector density. In (22)

$$\bar{\tau} - \bar{\eta} (y \nabla z - z \nabla y).$$



XV. *The Mechanical Forces indicated by Relativity in an Electromagnetic Field. Can their existence be demonstrated?* By ALEX. MCAULAY, M.A., Professor of Mathematics, University of Tasmania\*.

§ 1. **EQUATIONS** in C.G.S. measure.—In the paper "Multenions and Differential Invariants," III. (P. R. S.) the electromagnetic field was treated on the lines of relativity confined to a Riemann manifold, on a new and, I hope, simplified basis. The special conclusions therefrom are, in the present paper, brought to a much more satisfactory halting-stage than in the former paper.

First it is desirable to indicate (see synopsis below) the changes of notation necessary to pass from rational to C.G.S. units.

$t$  must everywhere be replaced by  $ct$  where  $c$  is the velocity of light in *vacuo*. This has to be remembered in every differentiation with regard to  $t$ ;  $\partial/\partial t$  must always be replaced by  $c^{-1}\partial/\partial t$ . There is one very important *apparent* exception to the statement that  $t$  is replaced by  $ct$ . Its cause may be thus stated. Merely to *preserve simplicity* in our mathematical expressions,  $f db$  and  $W db$  are no longer to be regarded as *elements of action*. They shall instead be taken to mean (action  $\times c$ ). Thus

$$f \cdot dx dy dz d(ct) = \text{action} \times c$$

and we derive the statement that

$$f \cdot dx dy dz dt = \text{action}.$$

This is the apparent exception referred to, since it may seem here to be exceptionally imposed that  $t$  remains unchanged instead of being replaced by  $ct$ .

$\mathbf{R}$  is written for the quaternion  $xi + yj + zk$ , or, according to our identifications (see § 3 below) for the multenion  $x\iota_2\iota_3 + y\iota_3\iota_1 + z\iota_1\iota_2$ ;  $\dot{\nu}$  as usual is used for  $\iota_1\iota_2\iota_3\iota_4$ . Thus

$$\rho = \iota_4(\dot{\nu}\mathbf{R} + ct)$$

in C.G.S. units, instead of  $\iota_4(\dot{\nu}\mathbf{R} + t)$  in rational units.

In C.G.S. units the  $\mathbf{H}$  of rational units must be replaced by  $(4\pi)^{-1}\mathbf{H}$ , but we do not require to introduce a single other  $4\pi$ .

The reader is recommended to think mainly of the E.M. system. Thus we shall write  $(c)$  and  $(c^{-1})$  for what in a completely comprehensive scheme would be written as

$$(c) = c\mu = c^{-1}K, \quad (c^{-1}) = (c)^{-1}.$$

\* Communicated by the Author.



In rational units, of course,  $D_t$  is written in place of the  $c^{-1}D_t$  of (7).

$\nabla$  is of dimensions  $L^{-1}$  and  $\omega \cdot \nabla$  of dimensions  $H^{-1}$ . Hence from the synopsis eqs. the dimensional relations are seen to be

$$HB = LF = (f), \quad X = L^{-1}H, \quad P = LB, \quad \dots \quad (8)$$

where  $(f)$  is the dimensional symbol of  $f$ . The reader will easily verify from these statements that all our equations are correct dimensionally. *Note.*— $HB$  is in ordinary theory energy per unit of three-dimensional volume. Now for simplicity we desire  $\omega^*$ ,  $\omega^\times$  to be of the same dimensions as  $H$ ,  $B$  respectively; and also we desire to retain the simple equation

$$\omega^\times = -\omega \cdot \nabla f.$$

This requires  $f dx dy dz d(ct) = f db$  to be of dimensions  $c \times$  action as we prescribed above. It will be seen that our prescriptions have left the dimensions of  $H$  or  $B$  absolutely arbitrary; with regard to  $H$  and  $B$  we have prescribed *only* that  $HB$  is force per unit area, that is energy per unit volume (area and volume in the usual three-dimensional sense).

§ 2. *The stresses and forces in an electromagnetic field.*—In § 21 of "Mult. etc." III., in the equations (23 a), (19 a), and in the equations (24), (25), (26), when supplemented by the expressions (24 a), (25 a), (26 a), a vector, normal to  $\iota$ , occurs and is denoted by  $\xi \cdot \iota = \nabla f$ . We shall here denote it by  $\sigma^{\bullet \times}$ . The vector can be completely evaluated in terms of  $\omega^*$ ,  $\omega^\times$ .

From eq. (26), when supplemented, we have

$$2_\theta(\nabla f \cdot \alpha^\times = \theta^{-1} \alpha^\times \cdot f - \theta^{-1} V_1(V_3 \omega^\times \alpha^\times) \omega^* - \theta^{-1} \sigma^{\bullet \times} \cdot V_0 \iota \alpha^\times.$$

$2_\theta(\nabla f - f \cdot \theta^{-1} = \phi$  is self-conjugate, so that  $V_2 \xi \phi \xi = 0$ . Using this we obtain at once

$$V_2 \iota \theta^{-1} \sigma^{\bullet \times} = V_2(V_1 \xi \omega^*) \theta^{-1}(V_1 \xi \omega^\times). \quad \dots \quad (1)$$

Since  $\sigma^{\bullet \times}$  is normal to  $\iota$

$$\sigma^{\bullet \times} = V_1 \iota \theta V_2 \theta^{-1} \sigma^{\bullet \times}$$

or

$$\sigma^{\bullet \times} = V_1 \iota V_2(\theta V_1 \xi \omega^*)(V_1 \xi \omega^\times). \quad \dots \quad (2)$$

This is the really useful form of  $\sigma^{\bullet \times}$  since it gives in neutral form

$$(\text{neutral form}) \quad \sigma^{\bullet \times} = V_1 \iota V_2 \omega^* \omega^\times, \quad \dots \quad (3)$$

but if we please we can rid eq. (2) of  $\zeta$ , obtaining

$$\left. \begin{aligned} \sigma^{\bullet\bullet} &= \theta V_1 (V_1 \omega^{\times} \iota) \omega^{\bullet} - V_1 (V_1 \omega^{\bullet} \theta \iota) \omega^{\times} \\ &= \theta V_1 \omega^{\times} V_3 \iota \omega^{\bullet} - V_1 \omega^{\bullet} V_3 \theta \iota \omega^{\times} \end{aligned} \right\} \quad \dots \quad (4)$$

In Galilean coordinates we have from (3)

$$\sigma^{\bullet\bullet} = V_1 [V_2 (\mathbf{BH} + \mathbf{DE}) - \dot{V} V_2 (\mathbf{DB} - \mathbf{EH})] \iota \dots \quad (5)$$

[In § 3 below is explained in detail how readily to effect the reductions of this § 2. We have thought this procedure would render the main argument clearer.] Thus putting

$$\iota = \iota_4 (\dot{V} \mathbf{V} + 1) / \sqrt{(1 + \mathbf{V}^2)}, \quad \dots \quad (6)$$

so that  $\mathbf{V}$  is the velocity, we obtain

$$\begin{aligned} \sigma^{\bullet\bullet} \sqrt{(1 + \mathbf{V}^2)} &= \iota_4 \{ \dot{V} [V (\mathbf{BH} + \mathbf{DE}) \cdot \mathbf{V}] \\ &\quad + V [\mathbf{DB} - \mathbf{EH}] \cdot \mathbf{S} (\mathbf{DB} - \mathbf{EH}) \mathbf{V} \}. \quad \dots \quad (7) \end{aligned}$$

Eq. (19 a) reads

$$-l T_{(5)} \zeta = V_1 \kappa^{\bullet} \omega^{\times} - \nabla_9 V_0 \iota_9 \sigma^{\bullet\bullet} - \sigma_9^{\bullet\bullet} V_0 \iota_9 \nabla_9 \dots \quad (8)$$

Our most important deduction from this happens to be easy; so before treating (8) generally we will make this deduction. Let the coordinates be chosen so that  $\mathbf{V}$  is zero at the point considered and therefore  $\iota$  becomes  $\iota_4$ . In the neighbourhood of the point let the medium also be at rest; in other words let the point be in a rigid body (or, at any rate, a body wholly at rest). Thus  $\iota$  is the constant  $\iota_4$  and all its derivatives are zero; and  $-V_0 \iota \nabla = D_t$  and  $\mathbf{V}$  of (7) is zero. Thus the quaternion expression for the force per unit volume is

$$\mathbf{VKB} - \mathbf{ES} \nabla \mathbf{D} + D_t \mathbf{V} (\mathbf{DB} - \mathbf{EH}). \quad \dots \quad (9)$$

The third term expresses a hitherto unsuspected (I believe) mechanical force exerted by the field. Can any physicist verify its existence? In C.G.S. measure the term is

$$D_t \mathbf{V} (\mathbf{DB} - \mathbf{EH} / 4\pi c^2).$$

[This is a case of the remark that to pass to C.G.S. units  $D_t$  must be replaced by  $c^{-1} D_t$ .]

Returning to (8), since  $V_0 \iota \sigma^{\bullet\bullet} = 0$ ,

$$-\nabla_9 V_0 \iota_9 \sigma^{\bullet\bullet} = \nabla_9 V_0 \iota \sigma_9^{\bullet\bullet}.$$

Hence putting  $\sigma^{\bullet\bullet} = l \sigma^{\times}$  and  $\iota = \iota^{\bullet}$  (8) may be easily written in the invariantive form

$$-l T_{(5)} \zeta = V_1 \kappa^{\bullet} \omega^{\times} + V_1 (V_2 \nabla \sigma^{\times}) \iota^{\bullet} - \sigma^{\times} V_0 \nabla \iota^{\bullet} \dots \quad (10)$$

Each of the two terms in  $\sigma^x$  is separately normal to  $\iota$ . That this portion of the force is normal to  $\iota$  means that the corresponding portion of  $F_4 (= -SEK)$  is zero when the medium is taken to be at rest; that is, there is no unsuspected energy transformation of an electrical or heat generating nature, due to the new term in the mechanical force.

In interpreting (10) assume, at the point considered,  $\mathbf{V}$  to be zero, but neither  $D_t\mathbf{V}$  nor  $(\nabla_g, \mathbf{V}_g)$  to be zero. The middle term of (10) thus contributes the third term of (9) together with

$$\text{where } \left. \begin{aligned} &V[V(\mathbf{BH} + \mathbf{DE})]D_t\mathbf{V}' - \nabla_g S(\mathbf{DB} - \mathbf{EH})\mathbf{V}_g' \\ &\mathbf{V}' = \mathbf{V}/\sqrt{(1 + \mathbf{V}^2)} \end{aligned} \right\} \quad (9a)$$

The third term of (10) contributes

$$V(\mathbf{DB} - \mathbf{EH}) \cdot (-S\nabla\mathbf{V}' + D_t[1/\sqrt{(1 + \mathbf{V}^2)}]) \quad (9b)$$

In changing to C.G.S. units  $\mathbf{V}$  must, of course, be replaced by  $c^{-1}\mathbf{V}$ .

I imagine these terms depending on acceleration and time-rate of strain are much too small to be determined experimentally. The physicist who understands the meaning of three-dimensional vectors has been placed by the expressions above in a position to judge for himself.

In addition to the three terms (9), (9a), (9b), expressing the mechanical force when the medium is at rest there will, of course, be terms due to the coordinates of strain entering the expression for action. What has been established is that a *perfectly arbitrary* invariant function  $f(\omega^*, \varphi^*, \theta)$  occurring as the field terms in  $W$  (action per unit of four-dimensional volume), a *quite definite* force per unit volume (from which the arbitrary function has completely vanished) must exist. The function, of course, has its effects, but these are merely to fix the details of interrelation of  $\mathbf{B}, \mathbf{H}, \mathbf{D}, \mathbf{E}$ . This result seems very surprising. Perhaps relativity will give similar guidance when elasticity etc. has been brought under its treatment.

§ 3. *Transformation from multenion to quaternion forms.*—With our identifications, a real quaternion  $Q$  is taken to mean

$$\begin{aligned} Q &= at_2t_3 + bt_3t_1 + ct_1t_2 + g \\ &= ai + bj + ck + g = \mathbf{G} + g, \end{aligned}$$

and an imaginary quaternion  $\dot{\nu}Q'$  to mean ( $\dot{\nu} = \iota_1\iota_2\iota_3\iota_4$ )

$$\begin{aligned}\dot{\nu}Q' &= a'\iota_4\iota_1 + b'\iota_4\iota_2 + c'\iota_4\iota_3 + g'\iota_1\iota_2\iota_3\iota_4 \\ &= \dot{\nu}(a'\iota_2\iota_3 + b'\iota_3\iota_1 + c'\iota_1\iota_2 + g') = \dot{\nu}(G' + g'),\end{aligned}$$

$Q + \dot{\nu}Q'$  is a bi-quaternion (in Hamilton's sense). The general multenion  $q$  is expressed by means of two bi-quaternions  $Q + \dot{\nu}Q'$ ,  $P + \dot{\nu}P'$  and  $\iota_4$  thus

$$q = (Q + \dot{\nu}Q') + \iota_4(P + \dot{\nu}P').$$

Let  $a$  be an arbitrary real scalar and  $\mathbf{A}, \mathbf{B}$  arbitrary real vectors (of the quaternion system). Then we have the following scheme :—

Forms of  $V_c q$ ;  $c=0, 1, 2, 3, 4$ .

$$\begin{array}{lll}V_0 q = a & V_1 q = \iota_4(\dot{\nu}\mathbf{A} + a) & V_2 q = \mathbf{A} + \dot{\nu}\mathbf{B} \\ V_4 q = \dot{\nu}a & V_3 q = \iota_4(\mathbf{A} + \dot{\nu}a) & \end{array}$$

It is easy to pick out the five parts of  $q$  given by the last equation. Thus

$$\begin{aligned}V_0 q &= SQ, & V_1 q &= \iota_4(\dot{\nu}VP' + SP), & V_2 q &= V(Q + \dot{\nu}Q'), \\ V_4 q &= \dot{\nu}SQ', & V_3 q &= \iota_4(VP + \dot{\nu}SP').\end{aligned}$$

The one biquaternion furnishes the even parts and the other (the  $\iota_4$  biquaternion) the odd parts, thus

$$\begin{aligned}Q + \dot{\nu}Q' &= (V_0 + V_2 + V_4)q, \\ \iota_4(P + \dot{\nu}P') &= (V_1 + V_3)q.\end{aligned}$$

The imaginary  $\dot{\nu}$  and also  $\iota_4$  are both commutative with the quaternions, but they are anti-commutative with one another, or

$$\iota_4\dot{\nu} = -\dot{\nu}\iota_4.$$

As a general rule collect all the  $\iota_4$ 's at the left of a complicated quadri-quaternion expression, attending to change of sign at each passage of  $\iota_4$  past  $\dot{\nu}$ . Then use the scheme for further treatment.

These remarks receive illustration in the transformations of § 2.

$$V_1 \kappa \omega^\times = V_1 \iota_4 (\dot{\nu}\mathbf{K} + \mathbf{K}_4)(\mathbf{B} + \dot{\nu}\mathbf{E}).$$

Consulting the scheme under  $V_1$  we have from the bi-quaternion  $(\dot{\nu}\mathbf{K} + \mathbf{K}_4)(\mathbf{B} + \dot{\nu}\mathbf{E})$  to pick out the part of the

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form  $\dot{\mathbf{v}}\mathbf{A} + a$ , that is,

$$\dot{\mathbf{v}}(\mathbf{VKB} + \mathbf{K}_4\mathbf{E}) - \mathbf{SKE}.$$

The rest of the bi-quaternion merely gives  $\mathbf{V}_3\kappa\omega^\times$  with which we have no concern. Thus

$$\mathbf{V}_1\kappa\omega^\times = \iota_4(\dot{\mathbf{v}}[\mathbf{VKB} + \mathbf{K}_4\mathbf{E}] - \mathbf{SKE}).$$

Hence we have the first two terms  $\mathbf{VKB} + \mathbf{K}_4\mathbf{E}$  of (9).

Next deduce (5) from (3)

$$\begin{aligned}\sigma^{\times} &= \mathbf{V}_1(\mathbf{V}_2\omega^\times\omega^\cdot)\iota_4, \\ &= \mathbf{V}_1[\mathbf{V}_2(\mathbf{B} + \dot{\mathbf{v}}\mathbf{E})(\mathbf{H} + \dot{\mathbf{v}}\mathbf{D})]\iota_4, \\ &= \mathbf{V}_1[\mathbf{V}_2(\mathbf{BH} + \mathbf{DE}) - \dot{\mathbf{v}}\mathbf{V}_2(\mathbf{DB} - \mathbf{EH})]\iota_4.\end{aligned}$$

Next deduce (7) using the abbreviations

$$\begin{aligned}\mathbf{V}' &= \mathbf{V}/\sqrt{(1 + \mathbf{V}^2)}, \quad \mathbf{X} = \mathbf{V}(\mathbf{BH} + \mathbf{DE}), \quad \mathbf{Y} = \mathbf{V}(\mathbf{DB} - \mathbf{EH}), \\ 1/\sqrt{(1 + \mathbf{V}^2)} &= b,\end{aligned}$$

so that  $b$  is what is usually denoted by  $\beta$ . We have

$$\begin{aligned}\iota_4 &= \iota_4(\dot{\mathbf{v}}\mathbf{V}' + b), \\ \sigma^{\times} &= \mathbf{V}_1(\mathbf{X} - \dot{\mathbf{v}}\mathbf{Y})\iota_4(\dot{\mathbf{v}}\mathbf{V}' + b), \\ &= \mathbf{V}_1\iota_4(\mathbf{X} + \dot{\mathbf{v}}\mathbf{Y})(\dot{\mathbf{v}}\mathbf{V}' + b).\end{aligned}$$

From the biquaternion ( ) ( ) following  $\iota_4$  we have to pick out the part of form  $\dot{\mathbf{v}}\mathbf{A} + a$ . Thus

$$\sigma^{\times} = \iota_4[\dot{\mathbf{v}}(\mathbf{VXV}' + b\mathbf{Y}) - \mathbf{SYV}']$$

which is eq. (7).

Similarly (11) and (12) can be deduced from (10).

In conclusion it may be remarked that

$$a\iota_4 + b\dot{\mathbf{v}} + c\iota_4\dot{\mathbf{v}} + g$$

is itself a quaternion such that we may put

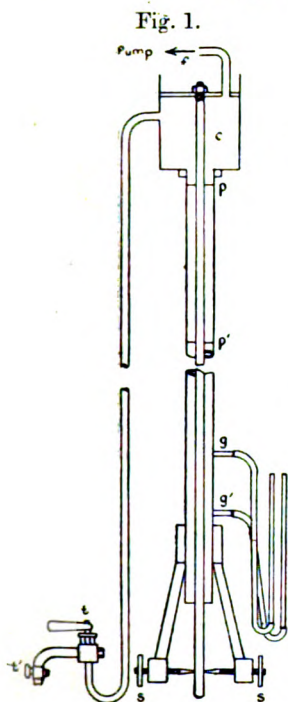
$$\iota_4 = i\sqrt{(-1)}, \quad \dot{\mathbf{v}} = j, \quad \iota_4\dot{\mathbf{v}} = k\sqrt{(-1)}.$$

University of Tasmania,  
28 November, 1922.

XVI. *The Flow of Water in the Annular Space between two Coaxial Cylindrical Pipes.* By THOMAS LONSDALE, B.Sc.\*

SEVERAL investigations have previously been made on the flow of liquids and gases in cylindrical pipes. So far as I know, no similar investigations have been made on fluids flowing in the annular space between two coaxial pipes. The present paper deals with an investigation for this special case. Preliminary experiments showed that it was necessary to have the pipes in a vertical position instead of the more usual horizontal one, owing to the impossibility of counter-acting the tendency of the inner pipe to sag inside the outer pipe when the pipes were in the latter position. The general nature of the flow was much the same as in the cylindrical pipe, there being a well-defined critical velocity separating regions of turbulent and non-turbulent flow.

*Apparatus and Method.*



The form of apparatus used is shown in fig. 1. The water was obtained from a tank in the roof of the laboratory, and the flow was controlled by the tap  $t$ , small variations being obtained by the means of side tap  $t'$ . From the tap the water passed into the canister  $c$  and then down the annular space. A filter pump  $f$  removed the air from  $c$  when starting up, and was thereafter kept running. Pegs  $p$  and  $p'$  attached to the inner cylinder served to centre it at the top and about a third of the way down, and the adjustable screws  $s$ , pointed so as to disturb the flow as little as possible and acting upon the protruded end of the inner tube, centred it at the lower end of the outer tube. The velocities of flow of the water were obtained by letting it run into a calibrated tank for a measured time.

\* Communicated by Prof. A. W. Porter, D.Sc., F.R.S.



The pressures at two points in the tube from which the pressure gradient was obtained were measured with the water manometers  $g, g'$ . It is remarked by Stanton and Pannell (Phil. Trans. Roy. Soc. A. 214) that in the case of flow in a pipe the length of "leading in" pipe through which the water must pass to enable irregularities of flow due to the inlet to be damped out varies from 90 to 140  $d$  where  $d$  is the diameter. In the present experiments the distance between the pegs  $p'$  and the first gauge hole  $g$  was about  $100(b-a)$  where  $b$  and  $a$  are the diameters of the outer and inner cylinders. The distances between  $g$  and  $g'$  and between  $g'$  and the orifice of the outer tube were about  $10(b-a)$ . The diameters of the cylinders experimented on are given in Table I. The two larger outer tubes were of smooth drawn brass and the smaller of smooth drawn copper. The 1.90 and 1.29 inner cylinders were tubes of a nickel-silver alloy mounted on mild steel shafting, and the .79 cylinder was a drawn phosphor-bronze rod.

No one material was found to have the necessary straightness in all the lengths and diameters required, and it was thought that the closer approximation to true annularity that was obtained by the use of varying materials, all smooth-drawn by the same process, would more than counterbalance the error due to possible differences created in the surface friction.

The gauge holes in the outer cylinder were made in the usual manner. The temperature of the water was observed by means of a thermometer placed in the water flowing to waste. In the preliminary experiments no effective difference was found between this temperature and that of the water in the canister. This temperature did not vary by more than  $.5^{\circ}$  C. throughout a set of observations. On each system, sets of observations on the relation between the pressure gradient and the mean velocity were taken in the directions of increasing flow and decreasing flow. During the preliminary work it was found that for low velocities tiny bubbles of air collected on the walls of the annular space. The rate of accumulation was small, but was enough to produce an effect equivalent to an increase in diameter of the inner cylinder. This seemed to be due to the siphon-like form of the apparatus. In order to obviate this difficulty, after each reading had been taken the tap was turned full on in order to drive all the air out, and was then adjusted until the gauges stood at their former levels. The flow was then increased or decreased according to the direction of procedure, and

another reading was taken. A slight modification was made in going in the direction of increasing flow from the non-turbulent to the turbulent region. In the neighbourhood of the critical velocity, after a reading had been taken and the air had been driven out, the flow was decreased until the gauges indicated a velocity well in the non-turbulent region. The flow was then very carefully increased until the previous gauge levels had just been passed, and the flow corresponding to the new level was measured. This was done in order to detect any persistence of stream-line flow which would give a critical velocity analogous to the second critical velocity of Osborne Reynolds (Phil. Trans. Roy. Soc. 1883). No such effect was observed. In the region just above the critical velocity where the gauges were very unsteady, the amplitude of movement was observed and the mean taken as indicating the pressure.

### *Discussion of Results.*

From the measurements taken we can obtain the law of variation of the pressure gradient with the velocity in the turbulent region, and a formula determining at what velocity turbulence will begin. We will consider these two parts in succession.

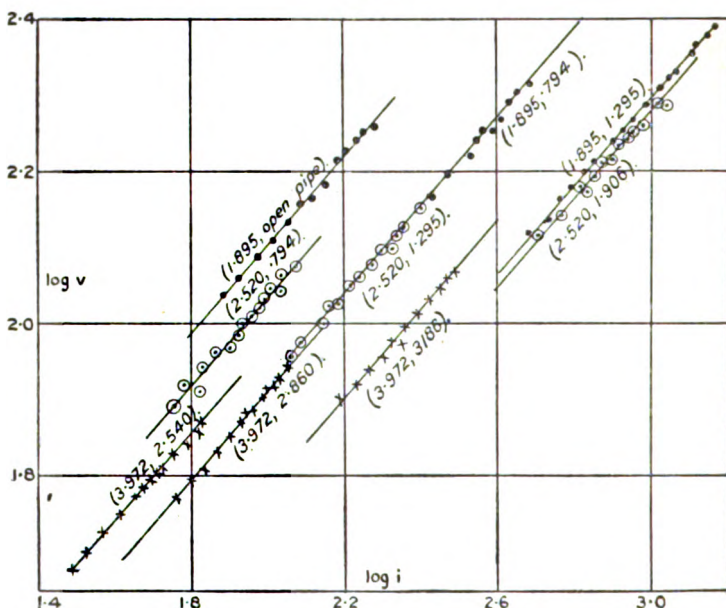
*Turbulent Region.*—On plotting the logarithms of pressure gradient and mean velocity in the turbulent region for each system, curves were obtained as shown in fig. 2. The figures in brackets beside each curve indicate the diameters of the outer and inner cylinders of the system for which the curve is a representation of the relation between the log pressure gradient and the log velocity.

Examination reveals the facts that the curves on the diagram are linear, and that the slope of the lines indicates that if  $i$  is the pressure gradient and  $v$  the velocity, then  $i = Cv^n$ , where  $n = 1.72$  and  $C$  is a constant for any particular system. Furthermore, from fig. 2 we see that the curves are nearly superposed for cases where  $b - a$  is nearly the same (where  $b$  and  $a$  are the diameters of the outer and inner cylinders respectively). This suggests that  $C$  contains a function of  $b - a$  as a factor; we will assume that a simple power function will suffice. An application of the method of dimensions leads to the expression

$$i = K(b-a)^{n-3} \mu^{2-n} \rho^{n-1} v^n,$$

where  $\mu$  is the viscosity and  $\rho$  the density of the liquid. This is of the usual form for an ordinary pipe where the range is sufficiently restricted for an index law to hold for the velocity, the only difference being that  $(b-a)$  replaces

Fig. 2.



the diameter of the pipe. In Table I. are shown the values of  $K$  calculated from my observations for the case  $n=1.72$ . Readings were also taken upon the 1.79 cm. ordinary pipe, in order to compare them with the results of other experimenters. The results in square brackets are computed for comparison from Stanton and Pannell's observations for smooth brass pipes (Phil. Trans. Roy. Soc. A. 214).

It will be seen that  $K$  for the 'systems' where  $b=2.52$  cm. is larger than in the other cases. This may be due to the 2.52 cm. pipe being slightly rougher than the other two outer pipes. It seems evident that the formula put forward gives a fair approximation to the experimental results. The mean value for  $K$  is .214. The units used are the G.C.S. system. The pressure gradient  $i$  is measured in dynes

TABLE I.

The Space between two Coaxial Cylindrical Pipes.				Ordinary Pipe.	
<i>b</i> .	<i>a</i> .	<i>b-a</i> .	<i>K</i> .	<i>b</i> .	<i>K</i> .
1.895	1.295	0.60	.212	1.895	.197
1.895	0.794	1.101	.206	[1.255]	[.210]
1.895	0.019	1.876	.199	[2.855]	[.213]
2.520	1.906	0.614	.228		
2.520	1.295	1.225	.231		
2.520	0.794	1.726	.225		
3.972	3.186	0.786	.211		
3.972	2.860	1.112	.197		
3.972	2.540	1.432	.217		

per cm.<sup>3</sup> and the velocity *v* in cm. per sec. The limits over which the formula has been tested experimentally should be made quite clear. The maximum velocities obtained were about 2.5 metres per second, and the largest pipe used had a diameter of 3.97 cm. The largest difference in diameters was 1.73 cm.

*Critical Velocity.*—In the non-turbulent region the relation between the velocity of flow and the pressure gradient is given by

$$v = \frac{1}{32\mu} i \left\{ b^2 + a^2 - \frac{b^2 - a^2}{\log \frac{b}{a}} \right\}^*$$

In the non-turbulent region this relation was found to be linear, as indicated by the formula, but when the critical velocity was just exceeded, the increase in *i* became large for a small increase in *v*, and the *i, v* curve bent sharply away from the straight line. Fig. 3 shows the type of curves obtained. The critical velocity is given quite definitely. In the case of the ordinary pipe this velocity *v<sub>c</sub>* is given by

$$v_c = \frac{K\eta}{d}, \text{ where } \eta \text{ is the "kinematical viscosity" or the}$$

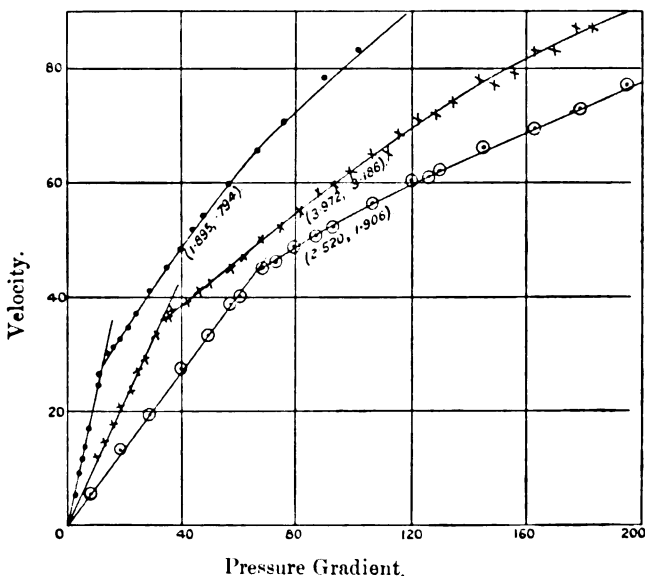
viscosity of the fluid divided by its density; *d* is the diameter and *K* is a constant. This constant varies according to the nature of the experiments and the materials of which the pipe is composed. In the papers previously referred to, Osborne Reynolds finds *K* = 2000 for drawn lead

\* Lamb, 'Hydrodynamics,' 4th edit. p. 579.

pipes, while Stanton and Pannell find  $K=2500$  for drawn brass pipes.

The principle of Dynamical Similarity (Stanton and Pannell, *loc. cit.*) can give us no information in the case of the flow of liquids in the annular space between two coaxial cylinders, because the linear dimensions of each system cannot be expressed by a single parameter corresponding

Fig. 3.



to the diameter in the case of the ordinary pipe. It is thus necessary to fall back on some purely empirical relationship to express the variation of the critical velocity with the diameters of cylinders in each system. For any one system  $v_c$  is found to vary directly with  $\eta$ , as in the case of the ordinary pipe. Experiments made on two systems in summer and winter showed that for a 30 per cent. change in  $\eta$  the ratio changed by less than 2 per cent.

For observations at the same temperature on different annular systems, it appears that at the critical velocity for any system the *quantity* of liquid is, roughly, directly proportional to the outer diameter of the system and independent of the inner diameter.

# Annular Space between two Coaxial Cylindrical Pipes. 169

Expressing this in symbols, we have  $v_c = K\eta \frac{b}{b^2 - a^2}$ , where  $K$  is a constant having the value just under 4000, and  $b^2 - a^2$  is proportional to the cross-sectional area.

The variation of the experimental results from any systematic empirical relationship does not justify the putting forward of a more elaborate expression. Table II. shows the experimental values of  $\frac{v_c}{\eta}$  for each system and the values given by the formula putting  $K=4000$ . Each experimental value represents the mean of eight determinations, which differed amongst themselves by about 5 per cent.

TABLE II.

$b$ in cm.	$a$ .	$\frac{v_c}{\eta}$ (experiment).	$\frac{v_c}{\eta}$ (formula).
1.895	1.295	3230	3970
1.895	0.794	2650	2560
2.520	1.906	3970	3700
2.520	1.295	2210	2160
2.520	0.794	1620	1760
3.972	3.186	2650	2820
3.972	2.860	1780	2090
3.972	2.540	1840	1790

The only serious divergence between formula and experiment, bearing in mind the variability of critical velocity measurements, occurs in the first line. This may be supposed to be due to a lack of axial symmetry in this system. Owing to the small diameter of the cylinders and the smallness of the annular space a divergence from axial symmetry is more likely to occur in this case than in any other, small diameter tubing being proportionally less straight than that of large diameter. The cases of the 1.89 open pipe and the (1.89, .019) system could not be investigated because the trumpet-shaped orifice stream became unstable and broke up before the critical velocity was reached.

In conclusion, I should like to express my thanks to Prof. A. W. Porter, F.R.S., for the many valuable suggestions that he has made and the encouragement that he has given me during the course of the work, and to my father, Mr. J. J. Lonsdale, D.Sc., for bearing the cost of the investigations.

XVII. *Movements of the Earth's Surface Crust, II.**By J. JOLY, F.R.S.\**

**I**N a recent paper appearing in this Journal (June, 1923) I dealt with a theory of the source of the surface changes experienced by the Earth over Geological time. In this present paper I propose to supplement the references to (a) the conditions of equilibrium leading to transgressional seas, and (b) the distribution of temperature in the continental crust.

*Transgressional Seas.*

In my former paper (*loc. cit.*) the development during inter-revolutionary times of a sub-oceanic crust was referred to. The conclusion was reached that such a crust might attain a thickness of some 15 miles (24 kilometres) in 25 million years.

Now the development of such a crust must have the effect of securing to the ocean a basal support extending nearly as far downwards into the substratum as the average basal level of the continental layer.

In order to arrive at this level we have to decide upon the most probable depth of the continental layer. Seismology has led to estimates between 30 and 35 kilometres. I shall take 32 k. If, now, we add the mean continental elevation (700 m.) to the mean depth of the ocean (4400 m.) and subtract from 32 k., we find the submergence of the continents in the substratum to be 27 k. The surface of the ocean floor is taken as the upper surface of the substratum. The base of the sub-oceanic crust is 24 kilometres below this level.

Now when fusion of the magma becomes widespread and its voluminal expansion lifts both ocean and continents together, there can be no general differential vertical movements due to loss of buoyancy, save in so far as the continental base may project into the magma below the general basal level of the sub-oceanic crust. This, on our present reckoning, will be only some 3 kilometres. It may be nil. But on the other hand, the deeply projecting

\* Communicated by the Author.

compensations will experience the effects due to the lessening density of the magma. They will grow heavier, as it were; the former isostatic equilibrium will be disturbed; and, locally, the continents will sink or sag downwards.

This effect will mainly take place where great mountain ranges and raised plateaux exist at the surface. Such transgressional flooding as affected the North American Continent during Laramide times would owe its initiatory development to this source. Similarly the earlier enlargement of the Mediterranean would be associated with the older mountain ranges then existing. In short, it is to such effects that we must ultimately ascribe the phenomenon of mountains begetting mountains. For such hollows must collect the debris of the millions of years which follow.

As the period of revolution approaches, the ocean floor begins to melt away and commingle with the general magma. Increasing circulation, both lateral and vertical, assails it with hot and, possibly, superheated currents. As it dwindles the continents become more and more exposed to the molten lava, and, as they had attained their former elevation relatively to the ocean at a period when the lava was at its maximum density, they must now experience as a whole the effects of the diminished buoyancy and begin to sink relatively to the ocean level. The ocean cannot experience this effect, but its floor may buckle or subside. To such movements the diminished rigidity of the suboceanic crust would contribute and, subsequently, the lateral compression to which it would be subjected; as referred to in my first paper. The deeps near continental margins are probable testimony to such compressional stresses. We possess unassailable evidence of vertical movements of the ocean floor even within recent times.

It is evident that with such a complexity of factors and without any sure knowledge of the amount and downward extent of the density change of the substratum, estimates of the differential vertical movements finally reached cannot be of value. It seems certain, however, as stated in my former paper, that the movements must be adequate to account for such estimates of the depths of transgressional seas as Geologists have been able to arrive at.

We possess, indeed, an indication of the prevailing relative densities of the submerged continental materials and the sustaining magma which is of special interest.

If it be accepted that the continental emergence is about 5000 m. and its submergence 27,000 m. then the ratio of



the density of the average submerged continental materials to that of the magma must be as 2·7 : 3·2 or as 2·53 : 3·0. A correction for the buoyant effects of the ocean will bring the ratio to about 2·65 : 3·0; which is in satisfactory agreement with the fundamental assumption that the continents do in fact, float on a substratum of basaltic magma.

In order to illustrate what has been said, let us consider the case of the continent of Africa. The mean height of that continent is stated to be 732 m. over sea level. The great plateau extending over its southern, central and eastern regions, possesses a mean altitude of 1332 metres. It, therefore, rises 600 m. over the general continental surface. If the density ratio of continental crust and magma is 2·6 to 3·0 we find that a compensating protuberance must extend nearly 4 kilometres into the magma to fulfil the condition that equal mass must underlie equal areas.

Now if the density of the substratum changes 10 per cent. a downward movement of the plateau region of 400 m. must occur to restore isostatic equilibrium. The force so originating will be supplemented by similar isostatic forces due to such compensations as may exist beneath the Atlas ranges and the Abyssinian region. The effects of the vertical stresses may be to depress the continent—possibly tilting it—so that transgressional waters will invade its low-lying regions. Thus the desert regions to the north-east, now at an altitude of about 300 metres over sea-level, would be flooded. Again they might possibly give rise to rifting of the continent in such direction as would most relieve the stresses. It seems probable that this is the sort of effect which must usher in a revolution.

One outcome of the foregoing views is the recognition of the fact, that cyclical changes of stress must, from the earliest times, have affected the earth's surface crust. During the period of advancing liquefaction the outer crust, as a whole, must experience stresses of tensile character. For the earth's surface is then increasing in area. When the climax of revolution is attained there must be a period of relaxation and recovery. Following this the shrinking of the substratum inaugurates a period of compressive stresses. This is the orogenic period as explained in my last paper. These stresses also die out and a long period of comparative repose attends the slow accumulation of radioactive heat in the substratum.

These cyclical changes of stress must have profoundly modified the surface features of the earth. They are the inevitable outcome of the existence of the substratum and the presence of radioactive elements throughout the materials of the earth's surface.

*The Distribution of Temperature in the Continental Crust.*

It follows from the principles of isostasy that the thickness of the continental crust must vary considerably ; extending downwards inversely as the greater surface features extend upwards. Taking the average density of the submerged continental materials as 2.6 and that of the substratum as 3.0 (*ante*), the compensations must extend downwards 6.5 times the elevation above the mean level of the raised surface features.

For the radioactivity of the continental crust we have a certain choice of data according as we take it to be of acid or of intermediate character. I shall assume that it possesses a radioactivity as if it were compounded of equal amounts of acid and intermediate rocks. This will be found to involve the development of  $0.27 \times 10^{-12}$  calorie per gram per second \*: If the density be 2.6 this becomes  $0.70 \times 10^{-12}$  cal. per sec. per c.c.

I shall first consider the question of the distribution of temperature in the average continental layer. In my last paper (*loc. cit.* p. 1174) I gave a computation showing that for a crust of 24 kilometres thickness, the steady output of radioactive heat must equal that indicated by the surface gradient. This is, however, defective not only in under-estimating the thickness of the continental layer but in under-estimating the heat flow indicated by the assumed surface gradient. It is, therefore, necessary to consider the question afresh.

If we adhere to our former estimate of continental thickness, i. e., 32 k. and take the average conductivity as  $4 \times 10^{-3}$  the basal temperature is found to be closely 900° C. (Strutt, Proc. R. S. 77 A). This, in the first place, is a sufficient approximation to the temperature of the substratum to meet the real point at issue :—that escape of heat through the continental stratum cannot take place to any considerable

\* Phil. Mag. Oct. 1912 & April 1915, also June 1923.

extent. With a temperature difference of only  $250^{\circ}$  the leakage would be small and would be closed by the growth of a thin basaltic crust congealed on the continental base. In point of fact had we assumed a continental thickness of 35 k. (which would have sufficiently satisfied the views of seismologists) and 'acid' radioactivity (also permissible), the calculated basal temperature would have come out as  $1225^{\circ}$ . The value selected above for the conductivity is the mean for granites, 'whinstones,' micaschists, and 'traps' as cited by Everett (C.G.S. System of Units).

We have now to consider how far this result may agree with gradients as observed in bore-holes, etc. over the continental surface. The heat coming to the surface originates in two ways. One part is generated by the radioactivity of the continental layer; the other ascends from beneath. The first is readily calculable (on data already cited) as  $224 \times 10^{-8}$  cal. per sec. per sq. cm. The second is  $31 \times 10^{-8}$  cal. per sec. per sq. cm. The total is  $2.55 \times 10^{-6}$  cal.

Thermal gradients, as all know, are very various—ranging from 26 to over 54 metres per degree centigrade. They steepen with depth so that in a distance downwards of 1000 metres they may steepen from 49 m. to 29 m.\* This fact, which is of general occurrence, shows that either some loss of sensible heat takes place or that, approaching the surface, the conductivity increases—as, for instance, due to presence of water.

This gain in conductivity due to moisture is exhibited in experimental determinations. We find dry sandstone reading 0.0055 and damp sandstone from 0.0064 to 0.0085 (Everett, *loc. cit.*). The mean of these figures and a gradient of 30 m. would account for a heat flow of  $2.5 \times 10^{-6}$  cal. per sec. per sq. cm. The conductivity of the damp sandstone may be excessive, but as we have taken but little account of the rise of gradient downwards it is plain that the thermal conditions arising out of a crust uniformly radioactive and at its base maintained at a temperature in or about  $1150^{\circ}$ , is not discordant with the indications of surface gradients.

We shall now turn to the question of the thermal stability of the greater compensations. I shall take as an extreme case that of the Tibetan Plateau. Its average height over sea-level is stated to be 15,000 feet or 4575 m. Its height reckoned from the average continental surface level of 700 m.

\* See Daly, Ann. J. Sc. May 1923.

is, therefore, 3875 m. Using the factor arising out of the density ratio as given above, *i. e.* 6.5, a compensation depth of 25,187 m. is obtained. Adding the continental depth and the height of the plateau, a total depth of 61 k. is arrived at.

What will be the distribution of temperature in so great a vertical depth of continental materials? The base is, say, at 1200°. The surface is at 0°. If the rise in temperature downwards exceeds at any level 1200° then there must be downward flow of heat. It is easy to see that this condition must come about. Hence there must be some level at which the direction of heat-flow changes, and this level must be that of maximum temperature. The equation connecting basal temperature with depth is  $\theta = \frac{Q}{2k} D^2$ , where  $Q$  is the heat generated in unit volume in unit time,  $k$  is the conductivity and  $D$  is depth. Accordingly the intersection of two parabolic curves, one displaced 1200° in the scale of temperature, may be used to determine the solution of problems of the present sort. We find that the level of maximum temperature is closely 42 k. from the surface and 19 k. from the base; the maximum temperature being 1500°.

From this we may infer that fusion must be nearly if not actually reached in this compensation. We might, of course, have chosen data which, while defensible, would give a lower internal temperature. But even as it stands it is doubtful if under the conditions of pressure actual fluidity would exist and not rather conditions of viscosity. Nor would a certain amount of fusion in such a case necessarily confer instability. For the fused interior would be on all sides shut in by a thick wall of stable material which, at least in periods succeeding revolution,—such as we now live in—must be but little hotter than the melting-point of the basalt and which being highly siliceous is, probably, mainly composed of quartz; the initial melting-point of which is 1600°.

However, even if in this particular case vertical forces could be transmitted through such a mass, it is certain that much deeper compensations would, on our data, be unstable. It is not improbable that herein we find a limit to isostatic compensation. It is stated that the Himalayas are only 80 per cent. compensated. Mountain elevation on the surface of the Globe would find limits from this cause. For observations appear to show that the rigidity of the crust is not able to carry the greater ranges without the support of compensations.

The whole matter is instructive. For the genesis of batholithic invasion from beneath, attending the rising mountain ranges,—which is one of the most striking and eloquent features of mountain structure—seems to find explanation in these simple calculations.

We may go even further. We saw above that the continental crust, taken at 35 k. thick, attains a radioactive basal temperature nearly the same as that of the substratum. Certain facts of petrological science possibly indicate that such a basal temperature would be greater than that of the magma. I refer to the evidence we possess that juvenile gases (notably water) contained in the abyssal magma might confer upon it a melting temperature somewhat lower than that which we observe in extravasated materials. If this be the case heat would flow downwards during the long era of general thermal accumulation throughout the substratum.

Now there must be a limit to such heat supplies to the magma: for under the continental base there is no escape for the heat till general fluidity is reached and the inevitable tidal movements distribute the heat into suboceanic regions. The superheated materials gravitating upwards must therefore accumulate beneath the continents, and if the temperature rises sufficiently, the base of the continental layer must melt; and when circulation and surface drift of the upper crust commence these melted materials must be carried from beneath the continents and float upwards around their margin.

These inferences seem to show that in the thermal conditions arising out of radioactive heating there arises a limit to continental thickness. Now this also controls the horizontal area of the continents, and, dependently, the area and depth of the ocean. For we see that if, originally, these lighter materials, rising like a scum to the surface of the magma, had been piled up deeper than they now are, either fortuitously or from forces originating in the rotational motion of the earth, they must inevitably have melted away beneath, until they attained their present thickness and surface extension.

June 1st, 1923.

XVIII. *On the Quantum Theory of the Complex Zeeman Effect.*By A. M. MOSHARRAFA, *Ph.D.*\*[Part of Thesis approved for the Degree of Doctor of Philosophy  
in the University of London.]§ 1. *Introduction and Aim.*

IN a previous paper †, a theory of the Zeeman Effect, for hydrogen, was developed from the standpoint of the Quantum Theory. In order to be able to extend the theory to other elements, a knowledge of the atomic fields for such elements would appear to be essential. Now, an exact theory of the atomic and molecular structures of the various elements may justly be described as the goal of Spectroscopic research. And, so far, it has only been possible to present such an exact theory in the case of the simple hydrogen atom. Nevertheless, the general theory developed by Sommerfeld ‡ for what he describes as the “non-hydrogen-like” elements, although it has no claim to absolute quantitative accuracy, yet leaves little room for doubt as to the relevance of its essential qualitative features. The aim of this paper is to show that a theory of the complex Zeeman Effect is possible which assumes the essential features of Sommerfeld’s theory of the atomic structure of the elements.

§ 2. *The Atomic Field.*

We assume with Sommerfeld § that the potential energy of an electron situated in the atomic field can be represented during the stationary states of the atom by

$$E_{\text{pot.}} = -\frac{eE}{r} + \frac{c_1}{r^3} + \frac{c_2}{r^5}, \quad . . . . (1)$$

where  $c_1, c_2, \dots$  are to be considered as small quantities of the 1st, 2nd, ... orders respectively,  $r$  being the distance of the electron [charge =  $(-e)$ ] from the nucleus of the atom which is taken as origin. There is no doubt that the origin of the terms in  $c_1, c_2, \dots$  is to be sought for in the electric forces between the electron in question and the other electrified particles entering into the structure of the atom.

\* Communicated by the Author.

† Roy. Soc. Proc., Series A, Feb. 1923.

‡ See A. Sommerfeld, ‘Atombau und Spektrallinien,’ II. Auf. Braunschweig, 1921, 4 Kap. § 6, p. 275.

§ *Loc. cit.*

And Sommerfeld\* has actually expressed these quantities approximately in terms of the specific conditions of a hypothetical ring of electrons (the "inner ring"), in which a number of electrons are assumed to be in uniform rotation round the nucleus, the radius of the ring being much smaller than  $r$ . He also writes  $E = ke$  = the total positive charge on the system (nucleus + "inner ring"), so that  $k$  is a whole number. Now, as Sommerfeld† himself points out, no account is taken in his theory of the reaction of the "outer" electron on the "inner ring." And Landé‡ has shown, in the case of helium, that if such account be taken, then  $E$  is no longer an integral multiple of  $e$ , but is given by

$$E = ke(1 + \kappa), \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where  $ke$  has the same meaning as before, and  $\kappa$  is a factor depending on the type of motion of the atom.

The quantities  $\nu$ ,  $c_1$ ,  $c_2$ , are accordingly here assumed in general to depend on the type of motion of the atom and to vary with it. We should, therefore, expect these quantities to involve not only the quantum numbers of the "outer" or, as we shall here call it, the Series electron, but also other "hidden" quantum numbers belonging to the rest of the atom. In discussing the steady states of the system, these quantities may, however, be legitimately regarded as mere constants.

It is important to note that we do not involve for the validity of our analysis any specific assumptions as to the origin of the correction terms in  $\kappa$ ,  $c_1$ ,  $c_2$ , ... etc. (such as Sommerfeld's "inner ring" hypothesis). For it is sufficient for our purpose:

- (i.) that the radiation from the atom in passing from one steady state to another may be regarded as corresponding to the change in energy of a single constituent electron, and
- (ii.) that the potential energy of this electron in the steady states may be considered to be given by equation (I) above.

These two hypotheses, which in effect form the essential features of Sommerfeld's analysis, are justified in some measure by the remarkable way in which they lead to the

\* *Loc. cit.* p. 506.

† *Loc. cit.* p. 279.

‡ A. Landé, *Physik. Zeitschr.* xx. p. 228 (1919), and xxi. p. 114 (1920).

Rydberg and Ritz forms of the Series term respectively as successive approximations.

With regard to the effect of the magnetic forces, arising from the motion of the rest of the atom, on the series electron, this may at once be dismissed as negligible. Such an effect would, of course, lead to a splitting of the spectral lines in a similar manner to the effect of an external magnetic field. The atomic magnetic field is, however, for

all ordinary elements of the order  $h = \frac{ev}{ac} (=) 10^3$  Gauss,

where  $v$  and  $a$  are comparable with the orbital velocity and atomic radius respectively. This would lead to a division of

the lines of the order  $\Delta\lambda = \frac{e\lambda^2 h}{4\pi m_0 c^2} (=) 10^{-3}$  Å in the visible

portion of the spectrum, where  $m_0$  is the mass of the electron and Å stands for Ångström units. The effect is thus too small to be detected, and we may safely dismiss it from our theory.

The effect of the change in the mass of the electron with velocity, on the other hand, is quite measurable. And although it does not play any special part in the Zeeman effect, we have nevertheless taken account of it in the analysis for the sake of completeness.

### § 3. Application of the Method of Separation of the Variables.

The analysis in this section is an extended form of our analysis in the last paper \*, the two main new features being : the existence of the two terms in  $c_1$  and  $c_2$  in the expression for the energy, and the possible variation of all the three quantities  $E$ ,  $c_1$ ,  $c_2$  with the external magnetic field  $H$ . The calculations are carried out to the second order of small quantities,  $c_1$  and  $c_2$  being considered of the 1st and 2nd orders respectively †. Powers of  $H$  beyond the first and products of  $H$  and second or higher order terms are neglected. The relativity correction terms are only taken account of to

the first power in  $\frac{1}{c^2}$  ‡, and their products with  $H$  or with second order terms are neglected.

Spherical polar coordinates  $(r, \theta, \psi)$  are used with the

\* *Loc. cit.*

† Cf. the beginning of § 2.

‡  $c$  is used throughout this paper to denote the velocity of light in vacuo; it is to be distinguished from the coefficients  $c_1$  and  $c_2$ .



origin in the nucleus and Oz in the direction of H. The notation is, as far as possible, kept the same as Sommerfeld's for facility of comparison.

Let W be the total energy of the series electron in one of the steady states of the atom, we have

$$W = E_{\text{kin.}} + E_{\text{pot.}} = m_0 c^2 \left( \frac{1}{\sqrt{1-\beta^2}} - 1 \right) - \frac{eE}{r} + \frac{c_1}{r^3} + \frac{c_2}{r^5},$$

where  $c\beta$  is the velocity of the electron. This may be written

$$\frac{1}{\sqrt{1-\beta^2}} = 1 + \frac{W + \frac{eE}{r} - \frac{c_1}{r^3} - \frac{c_2}{r^5}}{m_0 c^2}. \quad (3)$$

We also have

$$\begin{aligned} \beta^2 &= \frac{1}{c^2} (\dot{r}^2 + r^2 \dot{\theta}^2 + r^2 \sin^2 \theta \dot{\psi}^2) \\ &= \frac{1}{c^2 m^2} \left( p_r^2 + \frac{1}{r^2} p_\theta^2 + \frac{1}{r^2 \sin^2 \theta} p_\psi^2 \right), \end{aligned}$$

where

$$\left. \begin{aligned} p_r &= m\dot{r}, & p_\theta &= mr^2\dot{\theta}, & p_\psi &= mr^2 \sin^2 \theta \dot{\psi}, \\ m &= m_0 / \sqrt{1-\beta^2}, \end{aligned} \right\} \quad (4)$$

so that

$$\frac{\beta^2}{1-\beta^2} = \frac{1}{c^2 m_0^2} \left( p_r^2 + \frac{1}{r^2} p_\theta^2 + \frac{1}{r^2 \sin^2 \theta} p_\psi^2 \right),$$

or

$$\frac{1}{1-\beta^2} = 1 + \frac{1}{c^2 m_0^2} \left( p_r^2 + \frac{1}{r^2} p_\theta^2 + \frac{1}{r^2 \sin^2 \theta} p_\psi^2 \right). \quad (5)$$

From (3) and (5), we have

$$\begin{aligned} p_r^2 + \frac{1}{r^2} p_\theta^2 + \frac{1}{r^2 \sin^2 \theta} p_\psi^2 &= 2m_0 W + \frac{2m_0 e E}{r} - \frac{2m_0 c_1}{r^3} \\ &\quad - \frac{2m_0 c_2}{r^5} + \frac{1}{c^2} \left( W + \frac{eE}{r} - \frac{c_1}{r^3} - \frac{c_2}{r^5} \right)^2, \end{aligned} \quad (6)$$

which defines the total energy of the motion in terms of the Hamiltonian coordinates. Now

$$\frac{dp_i}{dt} + \frac{\partial W}{\partial q_i} = -e \sum_s \left( \frac{\partial \mathbf{A}}{\partial q_i} - \frac{\partial \mathbf{A}}{\partial q_s} \right) \frac{dq_s}{dt},$$

or

$$\frac{d(p_i - e\mathbf{A}_i)}{dt} \frac{\partial W}{\partial q_i} = -e \sum_s \frac{\partial \mathbf{A}_i}{\partial q_i} \frac{dq_s}{dt}, \quad (7)$$

where  $\mathbf{A}$  is the generalized vector potential given by

$$\left(\frac{\partial \mathbf{A}_1}{\partial q_2} - \frac{\partial \mathbf{A}_2}{\partial q_1}\right) = g_2 g_3 \frac{H_1}{c} \text{ and two similar equations, } (8)$$

subject to the condition

$$\sum_i \frac{1}{g_i} \frac{d}{dq} \left( \frac{\mathbf{A}_i}{g_i} \right) + \frac{1}{c^2} \dot{\Phi} = 0, \quad . . . (8a)$$

where  $\Phi$  is the scalar potential and  $g dq$  is lineal.

On applying (7) to the coordinate  $\psi$ , we get

$$\frac{d(p_\psi - e\mathbf{A}_\psi)}{dt} + 0 = 0,$$

so that

$$p_\psi - e\mathbf{A}_\psi = \text{constant} = F \text{ (say)}. \quad . . . (9)$$

Or, since

$$e\mathbf{A}_\psi = \frac{eHr^2 \sin^2 \theta}{2c} = m_0 w r^2 \sin^2 \theta, \quad . . (10)$$

where

$$w = \frac{1}{2} \frac{eH}{m_0 c}, \quad . . . . . (11)$$

we have from (9) and (10)

$$p_\psi = F + m_0 w r^2 \sin^2 \theta. \quad . . . . (12)$$

Substituting from (12) in (6), we have, on multiplying all the terms by  $r^2$  and rearranging them,

$$\begin{aligned} r^2 \left[ -p_r^2 + 2m_0 W + \frac{2m_0 e E}{r} - \frac{2m_0 c_1}{r^3} - \frac{2m_0 c_2}{r^5} \right. \\ \left. + \frac{1}{c^2} \left( W + \frac{eE}{r} - \frac{c_1}{r^3} - \frac{c_2}{r^5} \right)^2 - 2m_0 F w \right] \\ = p_\theta^2 + \frac{F^2}{\sin^2 \theta} + m_0 w^2 r^4 \sin^2 \theta. \quad (13) \end{aligned}$$

And in this last equation the variables are separable if we neglect the term in  $w^2$ , giving

$$\begin{aligned} r^2 \left[ -p_r^2 + 2m_0 W + \frac{2m_0 e E}{r} - \frac{2m_0 c_1}{r^3} - \frac{2m_0 c_2}{r^5} \right. \\ \left. + \frac{1}{c^2} \left( W + \frac{eE}{r} - \frac{c_1}{r^3} - \frac{c_2}{r^5} \right)^2 - 2m_0 F w \right] \\ = p_\theta^2 + \frac{F^2}{\sin^2 \theta} = p^2 \text{ (say)}, \quad (14) \end{aligned}$$

giving

$$p_r = \sqrt{\left[ A + \frac{2B}{r} + \frac{C}{r^2} + \frac{D_1}{r^3} + \frac{D}{r^4} + \frac{D_2}{r^5} \right]}, \quad (15)$$

$$p_\theta = \sqrt{\left( p^2 - \frac{F^2}{\sin^2 \theta} \right)},$$

where

$$\left. \begin{aligned} A &= 2m_0 W \left( 1 + \frac{W}{2m_0 c^2} - \frac{F_{1c}}{W} \right), \\ B &= e E m_0 \left( 1 + \frac{W}{m_0 c^2} \right), \\ C &= - \left( p^2 - \frac{e^2 E^2}{c^2} \right), \\ D_1 &= - 2m_0 c \left( 1 + \frac{W}{m_0 c^2} \right), \\ D &= - \frac{2e E c_1}{c^2}, \\ D_2 &= - 2c_2 m_0, \end{aligned} \right\} \quad (17)$$

omitting terms of higher orders.

We now apply Wilson's extended restrictions referred to in our last paper\*, viz.

$$\int_0^1 (p_i - e A_i) dq_i = n_i h, \quad i = 1, 2, 3, \dots \quad (18)$$

Thus, since

$$A_r = A_\theta = 0, \quad (19)$$

we have

$$\left. \begin{aligned} \int_0^1 p_r dr &= n_1 h \quad (\alpha), \\ \int_0^1 p_\theta d\theta &= n_2 h \quad (\beta), \\ \int_0^1 (p_\psi - e A_\psi) &= n_3 h \quad (\gamma). \end{aligned} \right\} \quad (20)$$

And on substituting from (9), (15), and (16), we get

$$\int_0^1 \sqrt{\left[ A + \frac{2B}{r} + \frac{C}{r^2} + \frac{D_1}{r^3} + \frac{D}{r^4} + \frac{D_2}{r^5} \right]} dr = n_1 h, \quad (21)$$

$$\int_0^1 \sqrt{\left[ p^2 - \frac{F^2}{\sin^2 \theta} \right]} d\theta = n_2 h, \quad (22)$$

$$\int_0^1 F d\psi = n_3 h. \quad (23)$$

\* *Loc. cit.* § 4, equation (17 a).

The first integral is evaluated in Appendix I. at the end of this paper. The second integral has already been evaluated in our last paper \*. The third integral extends over the period of  $\psi$ , namely from 0 to  $2\pi$ , and is thus at once seen to be equal to  $2\pi F$ . We have, using these results,

$$-2\pi i \left[ \sqrt{C} - \frac{B}{\sqrt{A}} - \frac{1}{2} \frac{B}{C\sqrt{C}} \left( D_1 + \frac{5}{2} D_2 \frac{B^2}{C^2} + \frac{15}{8} D_1^2 \frac{B}{C^2} - \frac{3}{2} \frac{BD}{C} \right) + \frac{3}{4} \frac{A}{C^2\sqrt{C}} \left( D_2 B + \frac{1}{4} D_1^2 - \frac{1}{3} CD \right) \right] = n_1 h, \quad (24)$$

$$p - F = \frac{n_2 h}{2\pi}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (25)$$

$$F = \frac{n_3 h}{2\pi}. \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

And from the last two equations we have

$$p = \frac{nh}{2\pi}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

where

$$n = n_2 + n_3. \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

In order to calculate the energy  $W$  of the static paths, let

$$W = W_0 + \delta W_w + \delta W_c, \quad . \quad . \quad . \quad . \quad (29)$$

where  $W$  is the value obtained for  $w = \frac{1}{c} = 0$  (*i. e.*, the value calculated in the absence of the field and without taking account of the relativity correction),  $\delta W_w$  and  $\delta W_c$  being first-order terms in  $w$  and  $\frac{1}{c^2}$  respectively; and adopt a similar notation for the coefficients  $A, B, C$ , etc. We have from (17)

$$\left. \begin{aligned} A_0 &= 2m_0 W_0, & B_0 &= eE_0 m_0, & C_0 &= -p^2, \\ D_{1,0} &= -2m_0 c_{1,0}, & D_0 &= 0, & D_{2,0} &= -2c_{2,0} m_0, \end{aligned} \right\} \quad (30)$$

\* *Loc. cit.* § 2, Part II., equations (46) to (50).

so that we have from (24) and (27)

$$-nh + \frac{2\pi i m_0 e E_0}{\sqrt{A_0}} - a_0 h + \frac{\alpha_0 A_0}{2m_0} = n_1 h, \quad \dots \quad (31)$$

with the following contractions :

$$a_0 = \frac{(2\pi)^4 m_0^2 e E_0}{n^3 h^4} \left( c_{1,0} - \frac{5}{2} c_{2,0} \frac{(2\pi)^4 m_0^2 e^2 E_0^2}{n^4 h^4} + \frac{15}{4} c_{1,0} \frac{(2\pi)^4 m_0^2 e^2 E^2}{n^4 h^4} \right) \quad \dots \quad (32)$$

$$= -3 \frac{(2\pi)^6 m_0^3}{n^5 h^5} \left( c_{2,0} e E_0 - \frac{1}{2} c_{1,0}^2 \right), \quad \dots \quad (33)$$

which leads to the Ritz form for  $W_0$  already obtained by Sommerfeld \*, viz.,

$$W_0 = - \frac{N h (E_0/e)^2}{(n + n_1 + a_0 - \alpha_0 W_0/h)^2}, \quad \dots \quad (34)$$

where  $N$  is the Rydberg constant

$$N = \frac{2\pi^2 m_0 e^4}{h^3} \dots \dots \dots (35)$$

With regard to the quantities  $E, c_1, c_2, \dots$  we assume † a change in their values due to the change in the type of motion of the atom produced by the magnetic field. We accordingly write

$$\left. \begin{aligned} E &= E_0 + \delta E, \\ c_1 &= c_{1,0} + \delta c_1, \\ c_2 &= c_{2,0} + \delta c_2, \end{aligned} \right\} \quad \dots \quad (36)$$

where  $\delta E/E_0, \delta c_1/c_{1,0}, \delta c_2/c_{2,0}$  are considered as first-order terms in  $w$ . The last of these quantities, however, will always occur in our analysis in terms already containing  $c_2$ , and may therefore be dismissed as beyond our degree of approximation. Thus, for our purpose,

$$c_2 = c_{2,0} \dots \dots \dots (37)$$

We can now write for the coefficients involved in (24) to

\* *Loc. cit.* p. 506.

† See § 2.

our degree of approximation

$$\left. \begin{aligned} A &= A_0 \left( 1 + \frac{\kappa}{W_0} + \frac{W_0}{2m_0c^2} + \frac{\delta W}{W_0} - \frac{Fw}{W_0} \right), \\ B &= B_0 \left( 1 + \frac{W_0}{m_0c^2} + \frac{\delta E}{E_0} \right), \\ C &= C_0 \left( 1 + \frac{e^2 E_0^2}{p^2 c^2} \right) = C_0 \left( 1 + \frac{e^2 E_0^2}{C_0 c^2} \right), \\ D_1 &= D_{1,0} \left( 1 + \frac{W_0}{m_0c^2} + \frac{\kappa}{c_{1,0}} \right), \\ D &= D_0 = \frac{e E D_{1,0}}{m_0 c^2}, \\ D_2 &= D_{2,0}, \end{aligned} \right\} \quad (38)$$

so that the values of the respective terms in (24) may now be written down

$$\left. \begin{aligned} -2\pi i \sqrt{C} &= 2\pi i \sqrt{C_0} \left( 1 + \frac{e^2 E_0^2}{2C_0 c^2} \right), \\ \frac{2\pi i B}{\sqrt{A}} &= \frac{2\pi i B_0}{\sqrt{A_0}} \left( 1 + \frac{3W}{4m_0c^2} - \frac{\delta W}{2W_0} \right. \\ &\quad \left. + \frac{\delta E}{E_0} - \frac{\kappa}{2W_0} + \frac{Fw}{2W_0} \right), \\ \frac{\pi i B D_1}{C \sqrt{C}} &= \frac{\pi i B_0 D_{1,0}}{C_0 \sqrt{C_0}} \left( 1 + \frac{2W_0}{m_0c^2} + \frac{\delta E}{E_0} + \frac{\delta c_1}{c_{1,0}} - \frac{3e^2 E_0^2}{2C_0 c^2} \right), \\ -\frac{3\pi i B^2 D}{2C^2 \sqrt{C}} &= -\frac{3\pi i B_0^2 D}{2C_0^2 \sqrt{C_0}} = -\frac{3\pi i e E_0 B_0^2 D_{1,0}}{2C_0^2 \sqrt{C_0} m_0 c^2}, \\ \frac{\pi i A D}{2C \sqrt{C}} &= \frac{\pi i A_0 D}{2C_0 \sqrt{C_0}} = \frac{\pi i A_0 e E_0 D_{1,0}}{2m_0 c^2 C_0 \sqrt{C_0}}, \end{aligned} \right\} \quad (39)$$

and the rest of the terms involved in (24) are not affected to our degree of approximation, either by the magnetic field or by the relativity correction.  $\delta W$  and  $\delta W$  are now obtained

by equating the sum of the terms in  $w$  and in  $\frac{1}{c^2}$  on the

right-hand side of (39) respectively to zero. We accordingly have

$$\delta W = \delta W_{\kappa, c_1} + \delta W_{\kappa, E} + \delta W_{\kappa, F}, \quad \dots \quad (40)$$

where

$$\left. \begin{aligned} \delta W_{\kappa, E} &= 2W_0 \left( 1 + \frac{D_{1,0}}{2C_0 \sqrt{C_0}} \right) \frac{\delta E}{E_0}, \\ \delta W_{\kappa, c_1} &= \frac{W_0 D_{1,0} \sqrt{A_0}}{C_0 \sqrt{C_0}} \frac{\delta c_1}{c_{1,0}}, \\ \delta W_{\kappa, F} &= Fw, \end{aligned} \right\} \quad \dots \quad (41)$$

which yield on substituting from (30) and remembering that  $\sqrt{C_0}$  must be taken as the negative (imaginary) root of  $C_0$ :

$$\left. \begin{aligned} \delta W_{\kappa, E} &= 2W_0 \left( 1 + \frac{im_0 \sqrt{2m_0} W_0}{p} c_{1,0} \right) \frac{\delta E}{E_0}, \\ \delta W_{\kappa, c_1} &= \frac{2im_0 W_0 \sqrt{2m_0} W_0}{p^3} c_{1,0} \frac{\delta c_1}{c_{1,0}}, \\ \delta W_{\kappa, F} &= Fw. \end{aligned} \right\} \quad \dots \quad (42)$$

And similarly we have for  $\delta W$  from (39) and (30) after some reduction

$$\delta W = \frac{2W_0 \sqrt{2m_0} W_0}{m_0 c^2} \left[ \frac{3W_0}{4 \sqrt{2m_0} W_0} - \frac{ieE_0}{2p} + \frac{3im_0 W_0}{p^3} c_{1,0} + \frac{3ie^2 E_0^2 m_0 c_{1,0}}{p^5} \right]. \quad (43)$$

Or, if we substitute the values of  $W_0$  and  $p$  from (34) and (27) respectively and introduce  $a_0$  as defined by (32), we have from (42) and (43) to our degree of approximation,

$$\left. \begin{aligned} \delta W_{\kappa, E} &= -\frac{2N_0' h}{(n+n_1)^2} \left( 1 - \frac{3a_0}{n+n_1} \right) \frac{\delta E}{E_0}, \\ \delta W_{\kappa, c_1} &= \frac{2N_0' h a_0}{(n_1+n)^3} \frac{\delta c_1}{c_{1,0}}, \\ \delta W_{\kappa, F} &= n_3 \frac{wh}{2\pi}, \end{aligned} \right\} \quad \dots \quad (44)$$

$$\delta W_c = -\frac{\gamma N'_0 h}{(n+n_1)^4} \left[ \frac{1}{4} (1-a_0 Z) + \frac{n_1}{n} \left( 1 - \frac{3a_0}{n+n_1} \right) \right], \quad (45)$$

where

$$N'_0 = N \times \left( \frac{E_0}{e} \right)^2, \quad . . . . . (46)$$

$$\gamma = \frac{(2\pi)^2 e^2 E_0^2}{c^2 h^2}, \quad . . . . . (47)$$

$$Z = 12(n_1+n) \left( \frac{2}{n^2} - \frac{1}{(n_1+n)^2} \right). \quad . . . (48)$$

#### § 4. Significance of the Results of the Previous Section.

We see from (44) that the exact value of  $W$ , and therefore the corresponding change in frequency  $\delta\nu$ , depends on the two variational terms  $\delta E/E_0$  and  $\delta c_1/c_{1,0}$  as well as on  $a_0$ .

The last quantity as given by equation (32) is identified in Sommerfeld's theory\* with the corresponding experimental quantity involved in the Ritz form of the Series term [see equation (34)], where  $n=1, 2, 3, 4 \dots$  are assumed to correspond to S, P, D, B ... terms respectively, i. e. to the variable terms in the II. Subordinate, Principal, I. Subordinate, Bergman, ... series. When, however, the values of the universal constants are substituted in (32), no satisfactory numerical agreement with experimental data is obtained, if we consider  $E_0, c_{1,0}, \dots$  as absolute constants. It is not our object in this paper to attempt an elucidation of this point. But we should like to point out that if  $E_0, c_{1,0}, \dots$  are regarded not as absolute constants but as depending on the type of motion of the atom (see § 2) and therefore involving unknown quantum numbers, and possibly  $n_1, n_2, n_3$  as well, then it would seem possible to attempt an explanation, not only of the numerical discrepancies in the values of  $a_0$ , but also perhaps of the doublet and triplet structures of the series†. This would, of course, involve a more or less exact

\* *Loc. cit.*

† No satisfactory explanation has so far been put forward of this fine structure. An additional atomic field arising from an electric doublet of charge  $e$  and moment  $M$  along  $Oz$  would lead to a fine structure expression,

$$\delta W = \frac{24\pi^4 m_0^2 e^2 M N'_0}{h^3 n^3 (n_1+n)^3} \left( 1 - \frac{n_1^2}{n^2} \right)^2,$$

which, however, does not give satisfactory agreement with observation (see a paper by F. Tank in the *Ann. d. Phys.* lix. p. 293, 1919). An explanation based on the relativity correction is equally unsuccessful



determination of  $E_0, c_{1,0}, \dots$  for the various types of atomic motions, a task for which our present theoretical equipments may not prove adequate. For our purpose here, however, it is not necessary to identify  $a_0$  with its corresponding experimental values.

With regard to the two variational quantities  $\frac{\delta E}{E_0}$  and  $\frac{\delta c_1}{c_{1,0}}$ , we are again led for their exact evaluation to a consideration of the motion of the whole atom and the variation of that motion with an external magnetic field. We may thus expect them to involve unknown quantum numbers as well as  $n_1, n_2, n_3$ . Now the order of magnitude, at least of those two variational quantities, is determinable from our analysis; for it must be the same as that of the other variational quantities involved (*e.g.*  $\frac{\delta W}{W_0}$ ). And it is the characteristic feature of our analysis that by assuming small variations of the energy coefficients  $E_0, c_{1,0}, \dots$  etc. proportional to the magnetic fields and of the same order of relative magnitude as the variations in the other constants of the original motion, we find it possible to arrive at a satisfactory explanation of the complex Zeeman Effect. We accordingly write:

$$\left. \begin{aligned} \frac{\delta E}{E_0} &= \frac{w(n+n_1)^2}{4\pi N_0'} \phi_1, \\ \frac{\delta c_1}{c_{1,0}} &= \frac{w(n_1+n)^2}{4\pi N_0'} \phi_2, \end{aligned} \right\} \dots \dots (49)$$

where  $\phi_1$  and  $\phi_2$  are functions of whole numbers.

From (40), (44), and (49) we have

$$\frac{\delta W}{W} = \frac{wh}{2\pi} \left( (n_3 - \phi_1) + a_0 \times \frac{(3\phi_1 + \phi_2)}{n + n_1} \right). \dots (50)$$

Now, Sommerfeld\* has shown that the splitting of the lines in the most general type of the Zeeman effect could be

(see end of our §4). The view I have here ventured to put forward that the structure of the series should depend on the type of motion of the atom would appear to receive support from the fact that the same element emits lines of different structural characters (doublets, triplets, etc.) under different experimental conditions, *e.g.* for its arc and spark spectra respectively.

\* *Loc. cit.* p. 537. See also a paper by the same author in the *Ann. d. Phys.* 1920.

exactly represented for any spectral line by the formula

$$\Delta\nu = \frac{w}{2\pi} \left( \frac{q_1}{r_1} - \frac{q_2}{r_2} \right),$$

where  $r_1$  and  $r_2$  (the "Runge denominators") depend only on the nature of the term to which they correspond (*i. e.*, whether S—, P—, D—, or B— term, etc.) and the structural character of the spectral line (*i. e.*, whether a simple line, a member of a triplet or doublet respectively), and  $q_1, q_2$  (the "Runge numerators") assume different values for the different Zeeman components out of the series 0,  $\pm 1, \pm 2, \dots, \pm r_1, \pm(r_1+1), \dots$  and 0,  $\pm 1, \pm 2, \dots, \pm r_2, \pm(r_2+1), \dots$  respectively. Also  $r_1 r_2 = r$ , the Runge number, which is fixed for each type of decomposition. The values of the Runge denominators for the respective terms are given by the following table, which we copy from Sommerfeld:—

TABLE A.

	S.	P.	D.	B.
Simple Lines .....	1	1	1	1
Triplet Lines .....	1	2	3	(4)
Doublet Lines .....	1	3	5	(7)

The table is based on the experimental results of Paschen and Back except for the two bracketed numbers, for which no corresponding experimental data are so far available and which have been written down by analogy. If we remember that the S, P, D, B terms etc. are characterized by the azimuthal quantum number  $n=1, 2, 3, 4$ , etc., we at once see from the table that the Runge denominator is numerically equal to 1 for simple lines,  $n$  for triplet lines, and  $2n-1$  for doublet lines.

We may therefore identify it with these numbers\* for the respective cases. And in order to arrive at an exact and full representation of the frequencies in the most general type of Zeeman decomposition, it is only necessary now to write from (50)

$$\left. \begin{aligned} n_3 - \phi_1 + \frac{a_0}{n+n_1} (3\phi_1 + \phi_2) &= \frac{n_3}{1} && \text{for simple lines,} \\ \text{or} &= \frac{\phi}{n} && \text{,, triplets,} \\ \text{or} &= \frac{\phi'}{2n-1} && \text{,, doublets,} \end{aligned} \right\} \quad (51)$$

\* The Runge denominators may not be identical with these numbers—*e. g.*, they may be given by functions of unknown quantum numbers, which functions must, however, be numerically equal to 1,  $n$ , and  $2n-1$  for the respective cases.

where  $\phi$  and  $\phi'$  assume values out of the series :

$$\begin{aligned} &0, \pm 1, \pm 2, \dots, \pm n, \pm (n+1), \dots \text{ etc.} \quad \text{and} \\ &0, \pm 1, \pm 2, \dots, \pm (2n-1), \pm 2n, \dots \text{ etc.} \quad \text{respectively.} \end{aligned}$$

From (51) we have as a first approximation for  $\phi_1$ , neglecting terms in  $a_0$  :

$$\left. \begin{aligned} [\phi_1]_0 &= 0 && \text{for simple lines,} \\ \text{or } &= n_3 - \frac{\phi}{n} && \text{,, triplets,} \\ \text{or } &= n_3 - \frac{\phi'}{2n-1} && \text{,, doublets.} \end{aligned} \right\} \quad (52)$$

Or, if we take account of terms in  $a_0$  to the first order only in (51), we may write

$$\left. \begin{aligned} \phi_1 &= [\phi_1]_0 + \frac{a_0 \sigma_i}{n + n_1}, \\ [\phi_2]_0 &= \sigma_i - 3[\phi_1]_0, \end{aligned} \right\} \quad i = 1, 2, 3, \dots \quad (53)$$

where the coefficients  $\sigma_1, \sigma_2, \sigma_3$  correspond to simple lines, triplets, or doublets respectively, but cannot be determined by our analysis, and the notation  $[ ]_0$  denotes values of the quantities involved calculated for  $c_{1,0} = c_{2,0} = \dots = 0$ .

The two functions,  $\phi$  and  $\phi'$ , introduced in (51) must be understood to involve "hidden" quantum numbers arising from a quantization of the general motion of the whole atom. The intensities and types of polarization of the various Zeeman components will depend on the nature of these two functions, and may be determinable by the application of Bohr's Principle of Correlation to the internal mechanism of the atom. Such an application would be equivalent to a form of Choice Principle relating to the "hidden" quantum numbers, and should lead to an explanation not only of the questions of intensity and polarization, but also of the way in which  $\phi$  and  $\phi'$  assume different groups of values for the different components of a doublet or a triplet.

With regard to the effect of the relativity correction on the appearance of the lines, we see from (45), (46), (47), and (48) that if we assume  $n$  to be fixed for each series term, then, since  $(n + n_1)$  is also fixed, it follows that  $n_1$  is also fixed, and hence  $\delta W$  is a one-valued quantity. Thus the effect of the

relativity correction on any spectral line would on Sommerfeld's theory \* consist in a slight modification in the position of the line given by

$$h\delta\nu = \delta W(m) - \delta W(n), \quad . \quad . \quad . \quad (54)$$

where  $\delta W(m)$  and  $\delta W(n)$  are given by (45) for the quantum numbers  $(m, m_1)$  and  $(n, n_1)$  respectively. This leads to no fine structure whatever, and an explanation of the doublet and triplet structure of the lines must be sought for elsewhere.

### § 5. Conclusion.

In his remarks on the array of figures given in Table A of the last article, Prof. Sommerfeld † writes : "only so much appears to be certain : that the harmony of integral numbers represented by our Runge Denominators has its ultimate foundation in the rules of hidden quantum numbers, and possesses a quantum derivation." We have attempted in this paper to inquire into the nature of this derivation, and have shown how it may be possible to ascribe the most complex and general types of Zeeman decomposition to small variations in the atomic field arising from the establishment of the external magnetic field. Our theory is, however, limited by our very deficient knowledge of the exact nature of the atomic field itself. The quantities  $E_0, c_{1,0}, c_{2,0}, \dots$ , etc. and the way in which they arise for the different types of atomic motions being only partly comprehended at present, it does not seem yet promising to attempt an evaluation of their variations with a magnetic field from first principles. Thus we have to satisfy ourselves in § 4 with the assumption expressed by equations (51), which may be regarded as empirical. This assumption may, on the other hand, be looked upon as a guide to the nature of the terms  $E_0, c_{1,0}, \dots$ , etc. themselves, and may eventually serve as a fresh test for possible theories which claim to assign exact values to these quantities from first principles. Thus the phenomenon of the Zeeman Effect may on the Quantum Theory, as it did on the classical theory, throw light on the problems of atomic structure and radiation.

\* *Loc. cit.*

† *Loc. cit.* p. 542 ; this is a free translation from the original, which is in German.

## APPENDIX I. (TO § 3).

To evaluate the integral

$$J_1 = \int_0^\infty \sqrt{\left[A_0 + \frac{2B}{r} + \frac{C}{r^2} + \frac{D_1}{r^3} + \frac{D}{r^4} + \frac{D_2}{r^5}\right]} dr. \quad (\text{i.})$$

This differs from the similar integral evaluated by Sommerfeld ('*Atombau, u.s.w.*' p. 476, under (e)) by the appearance of the term in D. We have to our degree of approximation

$$J_1 = J_2 + \frac{1}{2} D_1 J_3 + \frac{1}{2} D J_4 + \frac{1}{2} D_2 J_5 - \frac{1}{8} D_1^2 J_6, \dots \quad (\text{ii.})$$

where

$$J_2 = \int_0^\infty \sqrt{\left[A + \frac{2B}{r} + \frac{C}{r^2}\right]} dr = -2\pi i \left(\sqrt{C} - \frac{B}{\sqrt{A}}\right),$$

$$J_3 = \int_0^\infty \left(A + \frac{2B}{r} + \frac{C}{r^2}\right)^{-1/2} \frac{dr}{r^3} = +2\pi i \frac{B}{C\sqrt{C}},$$

$$J_4 = \int_0^\infty \left(A + \frac{2B}{r} + \frac{C}{r^2}\right)^{-1/2} \frac{dr}{r^4},$$

$$J_5 = \int_0^\infty \left(A + \frac{2B}{r} + \frac{C}{r^2}\right)^{-1/2} \frac{dr}{r^5} = -\frac{2\pi i}{2\sqrt{C}} \left(\frac{3AB}{C^2} - 5\frac{B^3}{C^3}\right),$$

$$J_6 = \int_0^\infty \left(A + \frac{2B}{r} + \frac{C}{r^2}\right)^{-3/2} \frac{dr}{r^6} = +\frac{3\pi i}{C\sqrt{C}} \left(\frac{A}{C} - 5\frac{B^2}{C^2}\right),$$

the values of all integrals except  $J_4$  being obtained from Sommerfeld's work, already referred to. To evaluate  $J_4$  we note that it is regular at infinity, so that

$$\begin{aligned} J_4 &= \int_0^\infty \frac{dr}{r^3} (C + 2Br + Ar^2)^{-1/2} \\ &= \frac{1}{\sqrt{C}} \int_0^\infty \frac{dr}{r^3} \left[1 - \left(\frac{B}{C}r + \frac{A}{2C}r^2\right) + \frac{3}{2} \left(\frac{B}{C}r + \frac{A}{2C}r^2\right)^2 + \dots\right] \\ &= -\frac{2\pi i}{\sqrt{C}} \left[\frac{3B^2}{2C^2} - \frac{A}{2C}\right]; \end{aligned}$$

and we finally have from (ii.)

$$\begin{aligned} J_1 &= -2\pi i \left\{ \sqrt{C} - \frac{B}{\sqrt{A}} \right. \\ &\quad - \frac{1}{2} \frac{B}{C\sqrt{C}} \left( D_1 + \frac{5}{2} D_2 \frac{B^2}{C^2} + \frac{15}{8} D_1^2 \frac{B}{C^2} - \frac{3}{2} \frac{BD}{C} \right) \\ &\quad \left. + \frac{3}{4} \frac{A}{C^2\sqrt{C}} \left( D_2 B + \frac{1}{4} D_1^2 - \frac{1}{3} CD \right) \right\}, \dots \quad (\text{iii.}) \end{aligned}$$

$\sqrt{C}$  being (as pointed out by Sommerfeld) taken as the negative (imaginary) root of C. This is the result quoted in the text.

King's College, London,  
April 1922.

XIX. *The Auroral Spectrum and the Upper Strata of the Atmosphere. Preliminary Communication. By* L. VEGARD, *Doctor of Science, Professor of Physics at the University of Christiania* \*.

**D**URING recent years I have been investigating the auroral spectrum. In the winter 1912-13, I undertook an expedition to Bossekop in Finmarken †, the main object of which was to study the auroral spectrum. With a spectrograph which combined a considerable dispersion with a great power of light, I succeeded in photographing a few of the strongest lines in the blue part of the auroral spectrum, and it was proved that these lines belong to the so-called negative band spectrum of nitrogen.

During the winter of 1921, I continued investigations in Christiania, and here I made determinations of the green auroral line ‡. As the result of a number of measurements, I found the auroral line to have the following wave-length :

$$\lambda = 5578.0 \text{ (intern. units).}$$

Although the auroral line was determined with such an accuracy that the error is only a fraction of an Å unit, the origin of the line remained as mysterious as ever.

It was to be hoped that a more complete investigation of the whole auroral spectrum might give us some valuable information also with regard to the origin of the green line. But apart from this question, the determination of the auroral spectrum is a problem of the very greatest importance, on account of its bearing on the question regarding the constitution of the upper strata of the atmosphere and the nature of the cosmic electric rays producing the aurora borealis.

In the year 1921 the "Government Fund for Scientific Research" furnished me with the necessary means for taking up this work in a more systematic way. A more complete description of experimental arrangement will be given in a later work. Presently I shall only mention that during the last winter (1922-23) three spectrographs, which were put up last summer, have been at work at the Geophysical Institute of Tromsø, where the top roof of the building has

\* Communicated by the Author.

† L. Vegard, *Phys. Z. S.* xiv. p. 677 (1913); *Ann. d. Phys.* l. p. 853 (1916); Bericht über eine Expedition nach Finmarke, *Christiania Vid. selsk. skr. Mat. kl.* 1916, No. 7.

‡ L. Vegard, *Geofysiske Publikationer*, vol. ii. No. 5. *Phil. Mag.* Ser. 6. Vol. 46. No. 271. July 1923.

kindly been put at my disposal by the Director, O. Krogness. For the sake of convenience we shall give the spectrographs the following notation, viz. I., II., and III. (Roman numerals), where

- I. is a quartz spectrograph with a fairly large dispersion and of high light power, for studying the ultra-violet part of the spectrum ;
- II. is a fairly big glass spectrograph with a considerable dispersion and a fairly high light power ;
- III. is a small glass spectrograph with the largest possible light power, but with a much smaller dispersion.

The spectrographs I. and II. were specially designed for an accurate determination of the wave-length of the lines that might appear in the auroral spectrum during the time of exposure, which had to be very long.

The small glass spectrograph, III., was constructed for the study of possible variations of the auroral spectrum, and also to learn how many lines could be observed in the visible part of the spectrum.

The big spectrographs I. and II. were mounted in a wooden box where the temperature could be regulated automatically. The whole box could be turned about a horizontal and a vertical axis.

These spectrographs have been in operation during the last winter (1922-23), and in this work I have been very ably assisted by Mr. Einar Tønsberg. We have already obtained a number of plates showing a considerable number of lines. The plates have been measured at the Physical Institute of Christiania, and in this work I have been ably assisted by Mr. Jonathan Aars.

With the quartz spectrograph we have obtained three spectrograms taken on "Imperial Eclipse" plates. The time of exposure and the lines obtained are given in Table I.

It appears that with a time of exposure of 15-20 hours of northlight a considerable number of lines can be obtained on the plate by means of the quartz spectrograph. It should be noticed that in the spectra 1 and 2 the strongest lines, such as 4278 and 3914, are over-exposed.

To give an idea of the relative strength of the lines, I have given them intensities from 1-10. Later on, I intend to give more accurate intensity values based on quantitative measurements with a registering micro-photometer.

On the spectrograms from the quartz spectrograph 21 lines have been measured.

TABLE I.

## Spectrograph I. (quartz spectrograph).

Photographic plates: "Imperial Eclipse."

Plate number.			Mean.	Intensity.
1.	2.	3.		
Time of exposure in hours.				
15.4	18.7	4		
$\lambda$ .	$\lambda$ .	$\lambda$ .	$\lambda$ .	
3134.4	3135.6	.....	3135.0	3
3160.4	3159.7	.....	3160.0	5
3208.3	.....	.....	3208.3	1
3284.9	.....	.....	3284.9	1
3371.5	3371.1	3371.2	3371.3	6
3432.7	(3431.2)	.....	3432.7	2
3467.8	(3466.7)	.....	3467.8	2
3502.9	.....	.....	3502.9	1
3535.7	3537.2	3535.5	3536.1	5
3575.6	3577.2	3577.8	3576.9	6
3710.7	3711.6	.....	3711.1	3
3756.3	3755.1	.....	3755.7	5
3805.2	3805.5	.....	3805.4	5
3911.6	3915.3	3914.5	3913.8	10
3997.5	3998.5	.....	3998.0	4
4054.3	4058.1	.....	4056.2	4
4239.1	4236.6	.....	4237.8	4
4277.3	4278.2	4277.6	4277.7	8
4421.5	.....	.....	4421.5	2
4653.1	4652.3	.....	4652.7	3
4708.6	4706.7	.....	4707.7	4

The spark spectrum of Cd used for comparison.

With the big glass spectrograph we at first used an Imperial panchromatic plate B. This plate was developed after an exposure of 20 hours of northlight, but the plate showed only the green auroral line. The He spectrum was used for comparison. The measurements gave for the auroral line the following wave-length :

$$\lambda = 5578.2.$$

Afterwards an Imperial Eclipse plate was put in, and developed after 18 hours of exposure. Only the six strongest lines in blue and violet were visible. The He comparison spectrum was over-exposed, and, in consequence, the accuracy of the wave-length determination may be somewhat reduced.



The measurements gave the following results :

$\lambda$ .
4708.7 Å
4651.1 „
4277.9 „
4266.8 „
4236.3 „
3913.3 „

The last line was very faint, so it could hardly be seen in the microscope. These are mainly the same lines as those which I observed in the year 1912-13. There is only the difference that now I get a faint diffuse line at about 4266.8, while in 1912-13 this line was not distinctly seen on the plate. A faint line, 4200, was just noticeable on one of my plates from the year 1912-13.

With the small glass spectrograph, III., the strongest lines (even with panchromatic plates) could be obtained with a time of exposure of 30-60 minutes.

TABLE II.

Spectrograph III. (small glass spectrograph).

Plate.						Mean.	Inten- sity.	Plate 17.
3 a.	3 c.	3 d.	4.	6.	7.			
Time of exposure in hours.								
0.8	0.8	0.5	1.6	1.4	0.8			6.8
...	[3745.5]	[3751.3]	...	...	...	...	1	3758.5
...	3810.6	3804.9	...	3800.8	...	3805.4	1	3807.0
3914.6	3913.3	...	[3908.3]	...	...	3913.9	10	3913.7
...	...	...	...	...	...	...	2	3941.5
...	3997.4	3999.1	...	3998.1	[4005.2]	3998.2	2	4000.4
...	4057.8	4058.4	...	4054.3	4051.9	4055.6	1	4059.7
...	...	...	...	...	...	...	1	4182.5
...	...	...	...	...	...	...	1	4200.0
4231.4	4239.1	4236.8	...	4235.8	4241.5	4236.9	5	4238.4
4278.5	4276.4	...	[4269.8]	...	...	4277.4	9	4279.0
...	...	...	...	4331.3	...	...	2	4345.8
...	...	...	...	...	...	...	1	4378.9
...	...	...	...	4424.7	...	...	2	4426.5
...	...	...	...	...	...	...	1	4478.5
...	...	...	...	...	...	...	1	4552.1
...	...	...	...	...	...	...	1	4591.9
...	4655.4	4653.7	...	4651.6	4651.4	4653.0	3	4650.8
4707.0	4713.3	...	...	...	...	4710.1	5	4708.3
...	...	...	...	...	...	...	1	4779.2
...	...	...	5582.8	...	5574.0	5578.4	1	4857.4

The spark of Cd used for comparison.

A considerable number of exposures have been made with this spectrograph, but only a few have been found sufficiently good for measurements, many of them showing only the same strongest lines that were more accurately determined with the two big spectrographs. But in order to see how many lines could be expected in the blue and violet part of the spectrum, a plate was taken (no. 17) which was exposed for 6.8 hours.

In Table II. are given the lines measured on some of the plates with a fairly small time of exposure. The last column contains the lines measured on the plate no. 17. As we can see, 20 lines have been measured, and probably some more lines can be traced by means of the micro-photometer.

An estimate of the intensities as they appeared on the plate no. 17 is also given in the table.

### *Identification of the Lines.*

The observations carried out in the year 1912-13 gave the result that the strongest lines in the blue part of the auroral spectrum were due to nitrogen and belonged to the so-called negative band spectrum.

Comparing the new lines found with those of the N spectrum, we at once see that nearly all of them must be ascribed to nitrogen.

On the left side of Table III. have been entered the auroral lines observed, and on the right side the corresponding N lines are given. In a column headed "Type" is given the type of spectrum to which the line belongs. The numbers and the classification are taken from H. Kayser, *Handbuch der Spectroscopie*. N.B. and P.B. mean negative and positive bands; L.S. means line spectrum.

All stronger lines in the ultra-violet found by means of the quartz spectrograph are quite accurately determined, and the errors less than 1 Å unit. The agreement between the auroral lines and the corresponding N lines is a very close one throughout the ultra-violet part—also the stronger lines of the visible part of the spectrum are quite accurately determined, and the identification quite certain.

The lines which are only determined by means of the small spectrograph may be somewhat less accurate, and there may be errors in the wave-length of 2-3 Å, but still I think the identification also of these lines is pretty certain.

TABLE III.

Auroral lines observed with spectrograph.			Lines of nitrogen spectrum.		
I.	II.	III.	$\lambda$ .	Type.	Observer.
3165.0 $\text{\AA}$	...	...	3135.9 $\text{\AA}$	P.B.	Hermesdorf.
3160.0 "	...	...	3159.2 "	"	"
3208.3 "	...	...	?	"	"
3284.9 "	...	...	3285.3 "	"	"
3371.3 "	...	...	3371.5 "	"	"
3432.7 "	...	...	?	"	"
3467.8 "	...	...	3468.1 "	"	Deslandres.
3502.9 "	...	...	3500.5 "	"	Hermesdorf.
3536.1 "	...	...	3536.8 "	"	"
3576.9 "	...	...	3577.0 "	"	"
3711.1 "	...	...	3710.7 "	"	"
3755.7 "	...	3758.5 $\text{\AA}$	3755.5 "	"	"
3805.4 "	...	3807.0 "	3805.1 "	"	"
3913.8 $\text{\AA}$	3913.3 $\text{\AA}$	3913.7 $\text{\AA}$	3914.4 "	N.B.	Deslandres.
...	...	3941.5 "	3943.1 "	P.B.	Hermesdorf.
3998.0 "	...	4000.4 "	3998.5 "	"	"
4056.2 "	...	4059.7 "	4058.7 "	"	Hasselberg.
...	...	4182.5 "	?	"	"
...	...	4200.0 "	4201.0 "	"	{ Hasselberg.
4237.8 "	4236.3 "	4238.4 "	4236.3 "	N.B.	{ Or N.B. 4198.8.
...	4266.8 "	...	4269.4 "	P.B.	{ Hasselberg.
4277.7 "	4277.9 "	4279.0 "	4278.0 "	N.B.	{ Diffuse line, perhaps
...	...	4345.8 "	4343.8 "	P.B.	{ shade of a band.
...	...	4378.9 "	4379.8 "	L.S.	{ Hasselberg.
...	...	4426.5 "	4426.2 "	"	{ Hasselberg.
4421.5 "(?)	...	4478.5 "	4478.0 "	"	"
...	...	4552.1 "	4552.3 "	"	"
...	...	4591.9 "	4590.0 "	"	"
4652.7 "	4651.1 "	4650.8 "	4651.2 "	N.B.	Neovius.
4707.7 "	4708.7 "	4708.3 "	4708.6 "	"	Hasselberg.
...	...	4779.2 "	4779.0 "	L.S.	"
...	...	4857.4 "	4860.6 "	"	Thalen.
...	5578.2 "	5578.4 "	?	"	Hemsalech.
5925 } bands.			{ Probably pos.		
6465 }			{ bands of N.		

We see that the auroral spectrum is almost entirely due to nitrogen. The lines partly belong to the negative, partly to the positive band spectrum, and in the visible part also some lines appear, which in the literature are arranged in the line spectrum.

The grouping of these lines may be a more or less artificial one. In the northlight spectrum, which corresponds to a fairly definite way of production, they appear mixed together and with a quite typical intensity distribution. In the northlight spectrum they may be said to form one family of lines.

In all, 35 lines have been measured : out of these, 29 lines have been identified as belonging to nitrogen, and the two lines or bands 5925 and 6465 are probably N bands. Still, however, the following four lines—the green line included—are not yet interpreted :

5578·2  
4182·5  
3432·7  
3208·3

These lines are not found among the recorded lines of the N spectrum. They cannot be ascribed to hydrogen, nor to helium or oxygen. I think there is little doubt that these lines also are due to nitrogen. This only means that the auroral spectrum is formed under conditions which are very difficult to reproduce in the laboratory. Several facts go to support this view, and I hope to gather some more knowledge through the continued work on the auroral spectrum.

A most important result of these observations of the auroral spectrum is that no indication of either hydrogen or helium lines has been observed. This fact is the more remarkable because in some of the spectra the stronger lines were greatly over-exposed.

During the last two years I have made experiments in my laboratory, the object of which was to study the light excited by the bombardment of cathode rays in mixtures of nitrogen and hydrogen, and nitrogen and helium. As a result of these investigations, which will be more fully treated later on, we can say that in mixtures N-H the presence of a few per cent. (3-7 per cent., say) of H can be detected in the spectrum when the N spectrum appears on the plate with about the same strength as that of the auroral spectrum. In mixtures of N and He the presence of 30 per cent. He can easily be detected.

It might be suggested that perhaps the energy possessed by the electric rays was sufficient for exciting the N spectrum, but too low to excite the H and He spectra ; if so, these gases might be present in the higher strata of the atmosphere and still give no light.

But such an explanation is not possible. The energy of

the rays must be less than that corresponding to a potential fall of 30 volts ; but whatever may be the nature of the cosmic rays, they must have a much greater energy if they get down to a height of 100 km. above the ground. Even if we only take into account the mass of nitrogen to be traversed, a cathode particle should have an energy corresponding to a fall through several thousands of volts, in order to get down to a height of 100 km., and any kind of positive rays would require a much higher voltage.

The absence of H and He lines in the auroral spectrum therefore shows that in that region where the auroral light is emitted, the pressure of H and He must be small compared with that of N in the same region.

Now, we know from observations of the height of aurora and the light distribution along the auroral rays \* that the principal part of the auroral light is emitted in the height interval of 100–120 km. Taking the mean value as representing the region of emission, we must have that at the height of 110 km. the nitrogen pressure must be at least 15 times as great as that of hydrogen and 3 times as great as that of helium.

The possible quantities of H and He which may be present will depend on the assumption we make with regard to the pressure distribution of nitrogen. Now, the quantity of nitrogen present at the various heights will depend on the way in which the temperature varies upwards.

In previous papers dealing with the absorption of electric rays in the atmosphere †, I have, in accordance with Wegener, assumed that the temperature up to a height of 10 km. on an average can be put equal to  $-23^{\circ}\text{C.}$ , and above this height put equal to  $-53^{\circ}\text{C.}$

In Table IV. is given the pressure at various heights ( $h$ ) for the gases H, He, N, and O, corresponding to the assumptions of Wegener.

At the height of 110 km. the pressure of nitrogen should be  $0.055\text{ dyn./cm.}^2$ , and for H and He  $10.25$  and  $0.494$  respectively. But if this value for the N pressure were nearly right, the auroral spectral analysis would show that the pressure of H and He could not be greater than  $0.0037$  and  $0.015$  respectively, or the hydrogen pressure could only be about  $4/10,000$ , and the He pressure only a  $4/1000$  part of that assumed by Wegener.

\* L. Vegard and O. Krogness, "The Position in Space of the Aurora Polaris," *Geophys. Publ.* vol. i. No. 1, p. 149.

† *Phil. Mag.* vol. xlii. p. 47 (1921).

TABLE IV.

$h$ . T=220.	$h'$ . T=300.	Pressure in dyn./cm. <sup>2</sup>			
		Hydrogen.	Helium.	Nitrogen.	Oxygen.
$400 \times 10^5$ cm.	$542.0 \times 10^5$ cm.	0.44	0.001	$4.4 \times 10^{-21}$	...
300 "	405.6 "	1.30	0.008	$1.69 \times 10^{-14}$	...
200 "	269.2 "	3.85	0.071	$6.5 \times 10^{-8}$	...
160 "	214.5 "	5.95	0.169	$2.8 \times 10^{-5}$	...
140 "	187.3 "	7.29	0.259	0.00058	...
130 "	173.7 "	8.24	0.321	0.0026	...
120 "	160.0 "	9.20	0.399	0.0121	0.0003
110 "	146.4 "	10.25	0.494	0.055	0.0013
100 "	132.8 "	11.4	0.611	0.251	0.0080
95 "	125.9 "	12.1	0.681	0.520	0.019
90 "	119.1 "	12.7	0.757	1.14	0.045
85 "	112.3 "	13.5	0.843	2.43	0.107
80 "	105.5 "	14.2	0.939	5.21	0.254
75 "	98.7 "	15.0	1.045	11.1	0.602
70 "	91.8 "	15.9	1.16	23.7	1.44
65 "	85.0 "	16.8	1.3	50.5	3.42
60 "	78.2 "	17.6	1.45	107.7	8.10
55 "	71.4 "	18.7	1.60	229.9	19.3
50 "	64.6 "	19.7	1.79	491.5	45.8

When the values of the pressures of H and He are given at 110 km., we can find the pressure at other heights, provided that we know the temperature. In Table V. is given

TABLE V.

$h$ . T=220.	Pressure in dyn./cm. <sup>2</sup>		
	Nitrogen.	Hydrogen.	Helium.
$400 \times 10^5$ cm.	$4.4 \times 10^{-21}$	0.00016	0.00004
300 "	$1.69 \times 10^{-14}$	0.00047	0.0003
200 "	$6.5 \times 10^{-8}$	0.0014	0.0026
160 "	$2.1 \times 10^{-5}$	0.0021	0.0063
140 "	0.00058	0.0026	0.0096
130 "	0.0026	0.0030	0.012
120 "	0.0121	0.0033	0.015
110 "	0.055	0.0037	0.018
100 "	0.251	0.0041	0.023

the variation of the H and He pressure above 100 km., provided that we put the pressure at 100 km., equal to 0.0037 and 0.018 for the two gases respectively. But we notice that going upwards the pressure of H and He will already, at a height of 120-130 km., overtake that of nitrogen. We

should get hydrogen and helium lines as soon as we got a bit further up. In consequence, we should expect to find a change in the appearance of the auroral rays when they are seen to pass from heights of, say, 3-400 km. down to about 110 km. But no such change is to be noticed. And it seems as if there should not be any possibility of the existence of a H and He layer in the upper strata of the atmosphere.

Now we may be aware of the possibility that our calculations of the nitrogen pressures are based on false assumptions with regard to the temperature distribution.

Recently a most interesting paper has been published by Lindemann and Dobson\*, dealing with the meteors. They have tried to calculate the amount of gas which a meteor must traverse in order to obtain the temperature necessary for its behaviour at the various heights.

They come to the conclusion that the density at a height of, say, 100 km. must be considerably greater than that ordinarily found, and they conclude that the higher strata must have a temperature of about 300° absolute.

Now we can easily calculate the pressures at various heights when we know the composition of the atmosphere 10 km. above the ground, and suppose that above this height the temperature is 300° absolute.

The pressure is found from a formula of the form :

$$p_h = p_0 e^{-\frac{h}{T} (k - k_0)} \quad \dots \quad (1)$$

Let  $h$  be 10 km., then  $p_0$  is the pressure at 10 km. If, now, we have calculated the pressure for one temperature, we can easily find the pressure distribution at another temperature in the following way :—

At the temperature  $T$  and a height  $h$  the pressure will be equal to that at a certain height  $h'$  at the temperature  $T_1$  provided that

$$\frac{h' - h_0}{T_1} = \frac{h - h_0}{T} \quad \dots \quad (2)$$

We have, in other words, by means of this formula to calculate the height  $h'$  which, for a temperature  $T_1$ , corresponds to a height  $h$  and a temperature  $T$ .

The heights  $h'$  corresponding to 300° are given in the second column of Table VI.

\* F. A. Lindemann and G. M. B. Dobson, "A Theory of Meteors and the Density and Temperature of the Outer Atmosphere to which it leads," Proc. Roy. Soc. A. cii. p. 411.



TABLE VI.

$h$ . T=300.	Pressure in dyn./cm. <sup>2</sup>		
	Nitrogen.	Hydrogen.	Helium.
542.0 $\times 10^5$ cm.	$4.4 \times 10^{-21}$	0.0053	0.00096
405.6 "	$1.69 \times 10^{-14}$	0.016	0.0077
269.2 "	$6.5 \times 10^{-8}$	0.046	0.068
214.5 "	$2.8 \times 10^{-5}$	0.072	0.162
187.3 "	0.00058	0.089	0.248
173.7 "	0.0026	0.099	0.308
160.0 "	0.0121	0.111	0.383
146.4 "	0.055	0.123	0.475
132.8 "	0.251	0.138	0.587
125.9 "	0.520	0.145	0.654
119.1 "	1.14	0.153	0.727
112.3 "	2.43	0.162	0.810
105.5 "	5.21	0.170	0.902
98.7 "	11.1	0.180	1.004

If, now, in the same way as before, we apply the results from our auroral spectral analysis on the distribution of nitrogen, which corresponds to  $T=300^\circ$ , we get the somewhat higher values for the possible pressures of H and He given in Table VI.

Also in this case, however, H and He would predominate above a height of 120–140 km.

As the ordinary hydrogen and helium lines are not to be found in the auroral spectrum, I think we can safely conclude that the green line (5578) cannot originate from any of these two gases, for this line remains the most prominent to the very bottom edge of all ordinary auroræ going down to a height of 95–100 km.

But at this height—as we saw—the pressure of H and He is very small as compared with that of nitrogen; and remembering that the N spectrum is very easily excited, it can hardly be assumed that a gas which is only present with a few per cent. in the mixture shall give the strongest line.

On the other hand, I have found by spectral observations that the green line is seen to the very top of the auroral ray streamers, and the gas which emits this line must be a prominent component of the atmosphere up to its extreme upper limits.

Hence we conclude that the hydrogen and helium layer, which has earlier been supposed to dominate at the top of our atmosphere, does not exist.

For the same reason we can hardly assume the existence



of some light unknown gas (geocoronium); for this gas had to be present at a height of 100 km., with a pressure of the same order of magnitude as that of nitrogen, in order to give the most prominent of all lines in the auroral spectrum. Being a light gas, however, geocoronium should soon predominate, and we should expect that any trace of a N spectrum should disappear at a height of, say, 140 km.

This conclusion is independent of the assumption we make about the temperature of the upper strata of the atmosphere, for if the temperature is high the pressure of N at a height of 100 km. will be greater, and for geocoronium we had to assume a correspondingly great pressure to make its green line predominant at this altitude. Somewhat higher up in the atmosphere the lighter gas (geocoronium) would take the lead.

If, then, we were able to show that in the auroral spectrum the nitrogen lines are maintained at a height greater than 150 km., I think we were justified in concluding that also the green line (5578) must be due to nitrogen. Observations are now in progress for testing this point.

From a physical point of view, however, it is very unlikely that a new gas (geocoronium) should exist, because there is no place for it in the periodic system.

I therefore think the best procedure would be to try to interpret the results of our spectral analysis without introducing the possibility of a new type of matter. The introduction of geocoronium is merely an easy way of getting out of the difficulty.

*But if we give up geocoronium, the green line must be ascribed to nitrogen, and nitrogen must be the predominant gas up to the very limit of the atmosphere.*

Here, however, we meet with a difficulty of another nature. From measurements of the height and position of the auroræ, we know that sometimes the upper end of an auroral ray can reach a height of 500–600 km., and at this height its light intensity is of the same order of magnitude as further down towards its bottom edge.

In previous publications\* I have dealt with the variation of light intensity along the ray streamers. The increase of intensity upwards can be explained by assuming that a greater part of the cosmic rays when they enter the atmosphere form great angles with the magnetic line of force. In this way we may explain that intensity variations along

\* L. Vegard and O. Krogness, 'The Position and Space of the Aurora Polaris,' p. 149. L. Vegard, Phil. Mag. xlii. p. 59.

the streamers may occur, but in order to get a noticeable intensity it is of course necessary that the pressure of the atmosphere does not fall below a certain limit.

From Table IV. we see that the nitrogen pressure decreases rapidly upwards. Assuming a temperature of  $220^{\circ}$  absolute above 10 km., the nitrogen pressure at a height of 400 km. should have the extremely small value of  $4.4 \times 10^{-21}$  dyn./cm.<sup>2</sup>

In this respect it does not help much to assume a somewhat higher temperature. With a temperature of  $300^{\circ}$  observed, the same low pressure would exist at a height of 542 km., which is also inside the auroral region.

If we at all are allowed to speak of a pressure of this order of magnitude, it would mean that at a height of 400–600 km., where the pressure is of the order  $10^{-21}$  dyn./cm.<sup>2</sup>, there should only be one molecule in a volume of 10 cubic metres. This, again, would mean that the density of the electric radiation had to be enormously great to produce the light intensity actually observed.

If, *e. g.*, we assume that the auroræ are produced by cathode rays of a certain velocity,  $v = \beta c$ , we can estimate the density of radiation by a comparison with the light produced when nitrogen is bombarded by a stream of cathode rays in a vacuum tube.

We suppose the sources of light to be placed before the slit of a spectroscopie at distances  $R$  and  $r$  from the slit. The effective cone of the instrument with a solid angle  $\omega$  cuts the sources in areas  $S$  and  $s$ . Let the intensity of light per unit area of the northlight and the vacuum tube be  $J_a$  and  $J_v$ . The quantity of light passing through the instrument in unit time will be proportional to

$$\frac{qSJ_a}{R^2} \quad \text{and} \quad \frac{qsJ_v}{r^2}$$

for the auroræ and the vacuum tube respectively ;  $q$  is the area of the slit, and

$$\frac{S}{R^2} = \frac{s}{r^2} = \omega.$$

If the two sources produce the same effect in the instrument, we get

$$J_a = J_v. \quad . \quad . \quad . \quad . \quad . \quad (3a)$$

Now, the intensity per unit area is equal to the intensity per unit volume multiplied by the thickness of the layer, because there is practically no absorption in the layer, at any

rate in the visible part of the spectrum. The condition of equal photographic effect then will be

$$i_a l_a = i_e l_e; \quad . . . . . (3 b)$$

$i$  is the intensity per unit volume,  $l$  is the thickness of the layer. The quantity  $i$  is proportional to the number of collisions made by the cathode particles per unit volume in unit time or proportional to  $\nu p$ , where  $\nu$  is the number of electrons crossing unit area in unit time. Let  $n$  be the number of cathode particles which at any moment is present in  $1 \text{ cm.}^3$ ; then

$$n = \frac{\nu}{v}.$$

Assuming the same ray velocity, the intensity of light emission per unit volume will be proportional to  $\nu p$ , and our condition for equal spectroscopic action take the form

$$n_a p_a l_a = n_e p_e l_e. \quad . . . . . (4)$$

For the vacuum tube we assume  $l_e = 1 \text{ cm.}$ ,  $p_e = 100 \text{ dyn./cm.}^2$ . The corpuscular current which would produce the same spectroscopic action as that of the upper part of an auroral ray can be estimated to about  $10^{-6}$  ampere when the velocity of the rays is about  $\frac{1}{2}c$ , where  $c$  is the velocity of light.

This would give

$$n_e e \beta = 10^{-7}.$$

Putting  $\beta = \frac{1}{2}$  and  $e = 4.8 \times 10^{-10}$ ,

$$n_e = 4 \times 10^2,$$

Hence

$$n_a p_a l_a = 4 \times 10^4;$$

$l_a$  is of the order of  $10^6 \text{ cm.}$ , and

$$n_a p_a = 4 \times 10^{-2}.$$

If, now,  $p_a$  were equal to  $4 \times 10^{-21}$ , it would follow that

$$n_a = 10^{19}. \quad . . . . . (5)$$

At any moment there should be about as many electrons (ray carriers) present in each  $\text{cm.}^3$  as there are molecules in  $1 \text{ cm.}^3$  of gas at  $0^\circ \text{C.}$  and atmospheric pressure. Such a density of electric radiation cannot be assumed. The electrostatic forces would prevent a ray bundle of such a density being formed.

If nitrogen is the predominant gas to the very limit of the atmosphere, it must at the height of 400–600 km. possess a density of a much higher order of magnitude than that previously calculated.

Quite formally we could get a sufficient pressure and density of nitrogen at a height of 600 km. by a proper assumption with regard to the temperature of the upper strata of the atmosphere.

If, as before, for the sake of simplicity, we suppose the temperature to be constant above 10 km. from the ground, we can easily find the temperature which is necessary to make the nitrogen pressure at 600 km. equal to a given pressure.

From Table IV. we see that for a temperature of  $220^{\circ}$  absolute, the pressure of nitrogen already at a height of 130 km. is only  $0.0026 \text{ dyn./cm.}^2$  If a nitrogen pressure of this magnitude should exist at a height of 600 km., the corresponding temperature  $T$  can be found from equation (2) by putting  $h=130$ ,  $h_0=10$ ,  $T=220^{\circ}$ ,  $h'=600$ ; and we get

$$T=1078^{\circ} \text{ abs.}$$

That the atmosphere above 10 km. should have a temperature of this magnitude must, I think, be considered as excluded.

The simplest way in which to prevent the nitrogen density from diminishing so rapidly as we pass upwards in the auroral region, would be to suppose that the upper strata were electrically charged, and consequently were acted on by electric forces. We might suppose the gas near the limit of the atmosphere partly to exist as positive ions. This is, in fact, what we should expect from a physical point of view. The upper layers of the atmosphere are exposed to the direct action of the sun's radiation. On account of the photoelectric effect, electrons will be driven out from the gas molecules with maximum velocities determined by the Einstein equation

$$\frac{1}{2}mv^2 = h\nu, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where  $\nu$  is the maximum frequency of the incident light, and  $h$  is Planck's constant.

Now it is pretty certain that the sun—besides the ordinary light spectrum—emits radiation of much shorter wave-length of the type we know from the X- and  $\gamma$ -rays. With energy quanta of this magnitude, electrons may be driven out of the atmosphere from quite a considerable layer of gas round the earth, leaving the gas molecules behind in the form of positive ions.

In this way a positively charged shell will be kept round the earth. Above a certain height the electric force will be directed upwards, and below this height it must, on account of the negative charge of the earth, be directed downwards.

The variation of pressure will no longer be given by the equation

$$dp = -\rho g dh, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

but instead of this we now get for higher strata

$$dp = -(\rho g - \sigma F) dh, \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where  $\sigma$  is the electric charge per unit volume and  $F$  the electric force. The electric charge will diminish the weight of a given quantity of gas; it will, as it were, make the molecules lighter. In this way we can understand that nitrogen in the auroral region can be distributed as if it were one of the very lightest gases.

Light gases like hydrogen and helium when they get ionized may have their weight so much reduced that they would fly away from the earth; and thus we may explain the absence of hydrogen and helium layers which have earlier been assumed to exist on the top of our atmosphere.

If the upper strata of the atmosphere to a great extent consist of positively-charged N molecules, we can also understand that under this condition the bombardment with electric rays may produce other N lines that we observe in our laboratory experiments, for it only means that we have not been able to produce artificially in the observation chamber a quantity of nitrogen containing a sufficiently large percentage of positive ions.

I also think that this hypothesis of an electrically-charged upper layer gives a very simple explanation to the results found by Lindemann and Dobson from their investigations of the meteors, for the greater density which they want will be produced by the electric charge of the upper layers, and we need not take refuge in the very improbable hypothesis of the high temperature which they suppose to exist above 10 km.

The highly ionized state of the atmosphere must be restricted to a certain layer, and as long as the cosmic rays are absorbed in this layer, we get the ordinary auroral spectrum showing the typical green line. As the typical greenish-yellow auroræ may have their bottom edges so far down as 100 km. above the ground, this would mean that the positive layer should go down to a height which is not greater than 100 km.

If the penetrative power of the rays could be great enough to enable them to pass into the neutral atmosphere, the nitrogen spectrum would turn into the more ordinary type and the green auroral line should disappear.

As a change of spectrum must be accompanied with a change of colour, this hypothesis of an electrically-charged upper layer gives us new possibilities for explaining the marvellous changes of colour which the auroræ may display.

Thus I think that the peculiar colour of a drapery-shaped arc, which I observed at Bossekop, October 1912, may be simply explained in this way. From the upper limit to a distance of a few km. from the bottom edge the arc had the ordinary greenish-yellow colour, but at a certain height the colour turned into dark red. This red bottom edge was found simultaneously all along the arc, which extended across the sky from E.N.E. to W.N.W., and was observed at least 8 minutes.

It would be of great interest to measure the height of such forms to see if they come lower down than the ordinary green arcs; but these phenomena are very rare, and the height of such arcs has not yet been measured. If our view is right, however, such auroræ would show us where the neutral atmosphere begins.

The auroræ, however, also show colour changes of another type. Separate auroral streamers or ray bundles forming part of a drapery or drapery-shaped arc may turn into another colour, usually red or bluish-red. The colouring is in this case not restricted to the bottom edge and is not kept for a considerable time, but it extends to almost any part of the streamer, and sometimes the whole ray bundle may turn red.

The red streamers appear in between the ordinary green-yellow ones; usually they only last for a fraction of a second. Other red-coloured bundles shoot in, and the distribution of colours, and thus the whole picture, will undergo very rapid changes.

To explain this kind of colour variation, I have in previous papers introduced the hypothesis that usually only a fraction of the rays that enter the atmosphere get absorbed, so that most of the rays return into space. Remembering that the spectrum from a gas bombarded by cathode rays depends on the velocity of these rays, we may expect to get a variation of colour according as a greater or smaller fraction of the rays are completely absorbed.

Some of the colour changes may no doubt be caused in this way; but if the upper layer of the atmosphere is positively charged, there will also be another possibility for colour changes to take into consideration.

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P

If a very intense ray bundle (consisting of negative electrons) pass through the positively-charged layer, and if it keep its position for some short time, the gas on its way may for a moment become partly neutralized, and the N spectrum may partly turn into the ordinary type corresponding to neutral nitrogen and which gives the red colour.

It is of interest to notice that the latter explanation of colour changes would require negatively-charged cosmic rays. In fact, the existence of a positively-charged upper layer of gas would involve that, at any rate, all auroræ showing a ray structure must be produced by rays of negative electrons. For, as we saw, the electrical charge of the layer would increase the density of matter throughout the auroral region. The mass of gas in a cylinder of unit cross-section reaching from a height  $H$  to infinity will be

$$m_H = \int_H^\infty \rho \, dh. \quad . \quad . \quad . \quad . \quad . \quad (9)$$

For a neutral gas we have  $m_H = \frac{p_H}{g}$ ; but this relation does not hold for an electrically-charged layer. Integrating the equation (8), we get

$$-\int_H^\infty d\rho = g \int_H^\infty \rho \, dh - \int_H^\infty F \sigma \, dh, \\ m_H = \frac{p_H}{g} + \frac{1}{g} \int_H^\infty F \sigma \, dh. \quad . \quad . \quad . \quad . \quad (10)$$

This equation shows that the mass  $m_H$  which a ray has to penetrate to get down to a height  $H$  is now greater than that calculated for neutral nitrogen (Table IV.); and if the charge is to produce a sufficient density of nitrogen 600 km. above the ground, the mass  $m_H$  at the height of 100 km., say, must be very much greater than that found for neutral nitrogen.

Any electric ray with a carrier of atomic dimensions which had a penetrating power great enough to enable the ray to get down to a height of 100 km., would possess a magnetic deflectibility, which would be too small to explain the narrow ray streamers.

Only electron rays combine a sufficient penetrating power with a sufficient magnetic deflectibility to explain the height and structure of the aurora \*.

Physical Institute, University,  
Christiania,  
March, 1st, 1923.

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*XX. The Theory of the Abnormal Cathode Fall.*

*To the Editors of the Philosophical Magazine.*

GENTLEMEN,—

I HAVE read with great interest a paper on the above subject published in this journal last month by the Research Staff of the General Electric Company whom I shall, for the convenience of this letter, identify with Mr. Ryde as his name is associated with the work. In consideration of the fact that the theory put forward is based almost entirely upon measurements made by me, I feel justified in making a few comments to caution the reader that its novelty of treatment and agreement with experiment are more apparent than real.

Under the more usual title of "Dark Space" I studied this fascinating phenomenon continuously for ten years, and I am entirely unable to accept Mr. Ryde's view that this simple theory is adequate even for a preliminary survey of the facts. To mention two minor points at the outset, I cannot see how a theory depending solely on the mass of the positive ions can give two entirely different results in the cases of  $N_2$  and CO since we expect, and positive ray analysis proves, that the mean mass of the positive ions is practically identical in both. Again, with the definite stated conditions under which all my measurements were made, I never found the slightest evidence of a measurable potential

\* *Note added to the Proof.*—Since I wrote this paper observations have been made with regard to the auroral spectra emitted at various altitudes, and investigations have been continued regarding the constitution of the upper strata of the atmosphere.

These investigations have led to the view that a highly ionized upper layer cannot exist in the form of gas—but we must assume the charge mainly attached to clusters—or small crystals of nitrogen. These investigations will be dealt with in a second paper.

At present I should only like to point out that in an upper layer formed by dust particles more or less electrically charged we can no longer apply the gas equations (1), (7), and (8). The conclusions based on the assumption that these equations hold for the auroral region therefore ought to be reconsidered.



difference between the metal of the anode and the edge of the negative glow. If such exists, direct experiments show that it cannot be more than a few volts, which will not go far to explain the discrepancy of about 130 volts shown by Mr. Ryde's parallel curves.

In the first paper I published on the subject in 1907 I gave a simple theory, which Mr. Ryde appears to have overlooked, founded on precisely the same premises as his, namely, that the boundary of the negative glow could be regarded as a highly conducting plane source of positive ions and that the density of electrons in the dark space could be neglected in comparison with that of the positive ions. The only difference between my theory and the one put forward is that I took for the velocity of the positive ions the expression for their mobility at ordinary pressures, whereas Mr. Ryde takes that of the free fall *in vacuo*. When I formulated my theory I had the choice of either of these expressions, but considered the latter certain to give too high a result. In this choice I have since been justified, for the difficulty is in making the velocity *low* enough to fit the facts. My theory required  $id^3V^{-2}$  to vary inversely as the pressure, which agreed very well with the numerical results obtained, but I abandoned it without any hesitation on ascertaining the law of distribution of potential in the dark space in 1911. The method by which the latter very simple but utterly baffling result was then demonstrated appears entirely free from objection. I have no more reason to doubt its substantial accuracy now than I had when I made the measurements, so that I find myself unable to consider very seriously any theory which does not attempt its explanation.

Equally formidable obstacles to the formulation of a workable theory are raised in my paper on the effect of the material of the cathode, where it is shown that a silver cathode gives twice the length of dark space given by a magnesium one and that with the same current and pressure the relation between  $V$  and  $d$  is accurately linear for six out of the nine metals tried. Further experiments with perforated cathodes carried out before the war but not published till 1919, showed that the phenomenon just in front of the cathode, far from being a simple hail of positively charged particles, was inextricably complicated by intense local ionization. I was therefore forced to the conclusion, which has been further strengthened by my subsequent work on positive rays, that no simple theory can explain the mechanism of the discharge in a satisfactory quantitative manner. It

seems in this way as intractable as an ordinary gas-flame, to which it bears many striking resemblances.

In conclusion, I may state that I now think that the true solution of all these perplexing discrepancies is probably to be sought for in the fact, now well established, that positive ions moving rapidly through a gas do not retain their identity but gain and lose electrons the whole time as they collide with other particles. The mechanism of these exchanges and its effect on the current carried is entirely unknown, but experiments of several different kinds are now focussed on this problem which should yield very valuable results in the near future.

F. W. ASTON.

June 7th, 1923.

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XXI. *On the Motion of Electrons in Gases.* By V. A. BAILEY, M.A., D.Phil., Demonstrator, The Electrical Laboratory, Oxford, Lecturer of Queen's College, Oxford \*.

1. **A** LARGE number of investigations have been made of the motion of electrons in gases, and it seems desirable to point out what reliable information may be obtained from the experiments, as the present generally accepted views of the behaviour of electrons in gases at the higher pressures and under low forces are to a great extent unsatisfactory. Too frequently the results of different experimenters do not agree with one another, or are obtained by a wrong interpretation of the observations; while in many cases the methods used are fundamentally unsound.

For values of the electric force  $X$  and gas-pressure  $p$  less than those for which ionization by collision occurs in notable quantities, the measurements are mainly concerned with  $W$  the velocity in the direction of the electric force, and  $K$  the coefficient of diffusion of charged particles in a gas. The particles may in general be either electrons or ions, but the motion of electrons is of special interest. The conditions under which ions are formed by electrons adhering to molecules have also been the subject of much discussion.

In some cases with ions the velocity  $W$  is found to be proportional to the ratio  $X/p$ . The constant of proportionality may then be termed the mobility of the ions, although the more common practice is to call  $W/X$  by that name, the gas being at atmospheric pressure.

\* Communicated by Prof. J. S. Townsend, F.R.S.

No useful object is served by extending this definition to those cases where  $W$  is not proportional to  $X/p$ .

Some experimenters have made the mistake of basing their experiments on the assumption that  $W$  is always proportional to  $X/p$ , without verification. Considerable errors have arisen from this cause, for in the case of electrons the velocity  $W$  is generally not proportional to the ratio  $X/p$ .

2. Methods \* for measuring  $W$  have been devised by Rutherford, Langevin, Zeleny, Chattock, and Townsend. The methods of Zeleny and Chattock are restricted to those cases where  $W$  is proportional to  $X$ , and the same is true of that particular type of Rutherford's method in which an alternating e.m.f. is used. But in Lattey's form of Rutherford's method and in Langevin's method no such restriction occurs, and reliable results may be obtained by them, except in those cases where diffusion effects are comparable with those due to the motion  $W$ . The effects of diffusion may be avoided by Townsend's method which is particularly suitable for determining the values of  $W$  for electrons.

The only methods of determining the coefficient of diffusion  $K$  are those due to Townsend, which are described in his book on 'Electricity in Gases,' Chapter V.

3. When in 1908 † it was shown for the first time that in dry gases (or even in moist gases, provided  $X/p$  is sufficiently high) the ions exist as free electrons having an abnormal energy of agitation as a result of elastic collisions with the gas molecules, it became at once an important matter to determine the velocities  $W$  corresponding to this novel state of affairs. This was done by Lattey ‡ for air, and by Franck § for argon and nitrogen, both using modifications of Rutherford's method.

In Lattey's form the charged particles coming through a gauze move under a constant electric force towards a parallel gauze for a known short interval of time  $t$ , and are then swept back again by reversing the field. No charged particles reach the second gauze until  $t$  is increased up to the value  $L/W$ , where  $L$  is the distance between the gauzes.

Franck made use of a sinusoidal alternating field in place of Lattey's constant field, so that his particles traversed the distance  $L$  with a variable velocity. He was thus compelled to assume that the velocity  $W$  was always proportional to  $X$ ,

\* Cf. J. S. Townsend's 'Electricity in Gases,' Chapter IV.

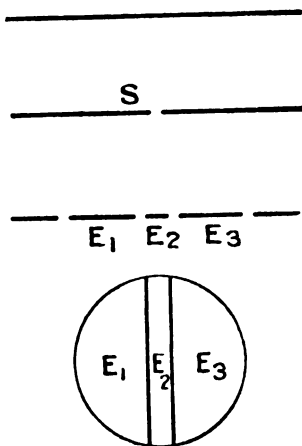
† J. S. Townsend, Proc. Roy. Soc. A. lxxx. p. 207, and A. lxxxi. p. 464 (1908).

‡ R. T. Lattey, Proc. Roy. Soc. A. lxxxiv. p. 173 (1910).

§ J. Franck, *Verh. d. Deut. Phys. Ges.* xii. pp. 291, 613 (1910).

which is shown very emphatically not to be generally true of electrons by Lattey's experiments and by the more recent experiments \* with Townsend's method. We shall see later that another disadvantage of the alternating field method is that it gives misleading information about the effect of impurities like oxygen which may form ions from free electrons.

There is a further source of error to which the Rutherford method is liable when used for studying the motion of free electrons, even when the constant field modification is adopted. A small group of electrons starting from a point near the first gauze do not all arrive simultaneously at the second gauze, but, owing to the effect of diffusion, the group spreads out in all directions as it moves, and electrons arrive at the gauze before the group as a whole traverses the distance  $l$ . Thus the observed time  $t$  will depend somewhat on the sensitiveness of the instruments used for detecting the first signs of electricity arriving at the second gauze, and also on the magnitude of the diffusion when compared with the velocity in the direction of the field.



Townsend's method of measuring  $W$  is, briefly, as follows: the ions or electrons (moving in a uniform field  $X$  throughout) pass through a narrow slit  $S$ , shown in the figure, and arrive on the electrodes  $E_1$ ,  $E_2$ ,  $E_3$ , which are separated by two narrow air-gaps. The centre of the stream falls on the centre of  $E_2$ . A suitable uniform magnetic field  $H$  is applied

\* J. S. Townsend and H. T. Tizard, *Proc. Roy. Soc. A.* lxxxviii. p. 336 (1913). J. S. Townsend and V. A. Bailey, *Phil. Mag.* xlii. Dec. 1921; xliv. Nov. 1922. M. F. Skinker, *Phil. Mag.* xlv. Nov. 1922.

perpendicular to  $X$  and parallel to the slit (or electrode  $E_2$ ), thus deflecting the centre of the stream towards one of the air gaps. The angle of deflexion  $\theta$  is known, and  $W$  can then be calculated by means of the simple formula  $HW/X = \tan \theta$ .

This method is free from the defects inherent to Rutherford's method which have just been considered, and is particularly well adapted to the case of free electrons, since the high values of  $W$  for these latter allow the use of moderate magnetic fields.

4. The evidence of the possible existence of free electrons in a gas was obtained by Townsend \* in the course of determinations of the quantity  $Ne$  † for different gases. He showed that in general this free existence depends on three main factors: the nature of the gas, its state of dryness, and the value of  $X/p$ . The larger the percentage of water-vapour present, the larger is the minimum value of  $X/p$  necessary to keep electrons in the free state, and even in pure water-vapour it is possible to maintain this condition of the electrons.

The experiments of Townsend and Tizard ‡ established that in very dry air the free electronic state exists when  $X/p$  exceeds the value 0.2, and the more recent experiments on very dry  $N_2$ ,  $H_2$ ,  $A$ ,  $He$  §, and  $CO_2$  || give similar results.

The case of  $O_2$  requires special mention, as there appears to be a general impression that small traces of this gas in any other gas will prevent the existence of free electrons. This conclusion appears to have been arrived at for the first time by Franck, and in support of it he gives the results of his mobility measurements for argon and nitrogen—namely, that the addition of 1.2 per cent. or more of oxygen to pure argon reduces the mobility of the negative ions from 206 to 1.7, and that a similar addition of oxygen to nitrogen reduces the mobility from 145 to 1.84. These conclusions as they stand are in agreement neither with Lattéy's experiments with air nor with those which were subsequently made by Townsend's method with air and oxygen. It appears from the investigations with oxygen that the electrons tend to combine with the molecules of that gas only at small values of  $X/p$ ; and the presence of the normal 20 per cent. of

\* J. S. Townsend, *loc. cit.* (1908).

†  $N$  = number of molecules in 1 c.c. of gas at  $15^\circ C.$  and 760 mm. Hg;  $e$  = charge on an ion.

‡ *Loc. cit.*

§ J. S. Townsend and V. A. Bailey, *loc. cit.*

|| M. F. Skinner, *loc. cit.*

oxygen in the air used by Townsend and Tizard did not appreciably affect the freedom of the electrons when  $X/p$  exceeded 2.

The erroneous conclusions of Franck may be attributed largely to the fact that the form of the Rutherford method which he used is very misleading for the purpose of investigating this point. The electrons in his apparatus moved in an alternating electric field, and were consequently in very weak fields for part of the time. It would be during this interval of time that the electrons became attached to the oxygen molecules, and as this would occur more or less at all values of the field amplitude, it would appear from these experiments that the oxygen molecule attaches electrons to itself under all conditions.

It may then be concluded that Franck's form of the Rutherford method is in general quite unsuitable for the study of the motion of electrons. Lattey's form of the method, however, is much less open to criticism, and fails to give accurate results only when the effects of diffusion become appreciable; but the method was originally designed for measuring the velocities of ions, and cannot be easily adapted to measure the higher velocities of electrons.

5. A rough general outline of the present state of knowledge about the motion of electrons in gases with low values of  $X/p$ , may be presented as follows. In order to obtain reliable values of the mean free path of electrons and the energy lost in collisions, it is necessary to determine experimentally both the velocity  $W$  in the direction of the electric force and the velocity of agitation  $u$  of the electrons. Theory and experiment agree in showing that when the electric force  $X$  and the gas-pressure  $p$  are varied so as to keep the ratio  $X/p$  constant, then the velocity  $W$  and the kinetic energy of agitation of the electrons remain constant, *i. e.*  $W = f(X/p)$  and  $k = \phi(X/p)$ , where  $k$  is the factor by which the kinetic energy of the electrons exceeds the kinetic energy of an equal number of molecules of gas at a standard temperature. The functions  $f$  and  $\phi$  are characteristic for each gas, but possess no simple mathematical form.

Regarding the equations  $W = f(X/p)$ ,  $k = \phi(X/p)$  as established experimentally, it is possible by means of them to find the mean free path  $l$  of the electrons in the gas (at some standard pressure), and the mean energy  $E$  lost by an electron at each collision with a gas molecule. Both  $l$  and  $E$  are functions solely of the mean velocity of agitation  $u$  of the electrons.

In those gases where the electrons can attach themselves

to the molecules under certain conditions, we may in the same manner consider that the probability of an electron adhering to a molecule is a function of  $u$  only. If in  $N$  collisions made by the electrons  $hN$  result in attachment, we may call  $h$  the probability of ion formation and may set  $h = F(u)$  where  $F$  is characteristic for each gas. Very little is known about  $h$ , except that it is practically zero for  $N_2$ ,  $H_2$ ,  $He$ ,  $A$ , and  $CO_2$ . Electrons may travel several centimetres through those gases, making several thousand collisions with molecules, and not become attached to them. In oxygen, water-vapour, and some other gases and vapours,  $h$  is not zero, except possibly for large values of  $u$ . In general, as appears from the experiments on ionization by collision,  $h$  is extremely small for large values of  $u$ .

This point of view differs from that of J. J. Thomson\*, who considers  $h$  to be constant for a given gas, and thus independent of  $u$ . It is impossible to reconcile Thomson's view with the above experimental facts about oxygen and water-vapour.

L. B. Loeb† has attempted to determine  $h$  for a number of gases on the basis of Thomson's theory and using Franck's method of measuring the "mobilities." But as Thomson's theory conflicts with a large amount of experimental evidence, and Franck's method of measuring "mobilities" is very unsuitable for dealing with a stream containing any electrons, Loeb's results cannot be regarded as being convincing.

## XXII. Notices respecting New Books.

*Physiology of the Ascent of Sap.* By Sir JAGADIS CHUNDER BOSE, M.A., D.Sc., F.R.S., C.S.I., C.I.E. Longmans, Green & Co. 1923. 16s. net.

IN this book Sir Jagadis Bose has collected together a series of the researches which he has been carrying out at the Bose Research Institution recently with the co-operation of a large number of research students. The problem of the ascent of sap has for a long time baffled researchers. The main difficulty of the problem resides in the lack of adequate means of detecting and measuring the rate of ascent of transpiration, exudation, and their induced variations. The elaborate and intricate instruments which

\* J. J. Thomson, *Phil. Mag.* i. p. 369, April 1901.

† L. B. Loeb, *Phys. Rev.* xvii. 2 (1921), and *Phil. Mag.* xliii. Jan. 1922.

have been devised by Sir Jagadis Bose have been further developed for the attack on this problem. Various types of automatic recorders of great sensitiveness and precision have proved of value: the electric probe has been used to localize phenomena occurring in the cells.

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### XXIII. *Proceedings of Learned Societies.*

#### GEOLOGICAL SOCIETY.

[Continued from vol. xlv. p. 799.]

December 20th, 1922.—Prof. A. C. Seward, Sc.D., F.R.S.,  
President, in the Chair.

THE following communications were read:—

1. 'A Micrometric Study of the St. Austell Granite (Cornwall).  
By William Alfred Richardson, M.Sc., F.G.S.

The problem of the effect of sampling a coarse-grained rock by means of slices is considered in detail, and to estimate this effect a statistical standard and the consistency of the mapped values are used.

Qualitative and quantitative study of the minerals reveals three types of rock: (a) a biotite-muscovite-granite of coarse grain confined to the east; (b) a lithionite-granite occupying by far the greater part of the outcrop; and (c) a gilbertite-granite confined to a small area near St. Stephen's Beacon, and furnishing the 'china-stone' rock.

The correlations of certain minerals are examined. A high negative correlation is found between quartz and orthoclase—true for this area, but not for granites in general. Almost complete correlation is indicated between topaz and minerals of the contact-group, while the correlation between biotite and tourmaline is hardly of any significance.

When mapped, the minerals fall into groups that show little relation to the boundaries of the granite as a whole, but are distinctly connected with the areas occupied by the different types. The minerals within the different areas are arranged in a similar way. There is an outer zone rich in quartz and to some extent in mica, surrounding an inner region noteworthy for a high content of orthoclase; while the plagioclase is sometimes concentrated centrally, and sometimes towards the margin.

There is evidence to show that the magma invaded the area progressively from the east to the west; and that it had always partly, and sometimes largely, crystallized before injection into the



present level. An explanation of the exceptional arrangement of the minerals, based on the motion of the invading magma, is suggested.

2. 'The Petrography and Correlation of the Igneous Rocks of the Torquay Promontory.' By William George St. John Shannon, M.Sc., F.G.S.

A description of the field relations is given, and it is demonstrated that two stages of vulcanicity occurred—in the Middle and in the Upper Devonian, as shown by basic tuffs and a spilite.

The intrusions form an alkaline suite. Albite-dolerite, with segregations, forms a laccolite at Black Head, and carries quartz and occasional olivine. Two isolated outcrops are correlated with this on petrographic grounds. Metasomatic silicification is ascribed to this intrusion. Evidence of the stability of the albitization and the subsequent alteration of augite to limonite is given; at the Red Rocks, Babbacombe, this approaches a laterite in character.

An augite-lamprophyre in limestone, and a soda-porphryrite in Middle Devonian slates are described from Babbacombe.

A preliminary account of the tectonics is attempted, particularly of the inversion, at Ilsham, of the faulting and of the north-to-south strike of some of the folds.

The results may be summarized as the recognition of the extension of the South-Western Alkaline Province; the existence of an alkaline intrusion, in addition to segregations; the Upper Devonian age of certain slates; and finally, the establishment of the apparent tectonic succession and post-Culm date of the folding.

January 10th, 1923.—Prof. E. J. Garwood, Sc.D., F.R.S., Vice-President; and afterwards Prof. A. C. Seward, Sc.D., F.R.S., President, in the Chair.

Prof. WILLIAM JOHNSON SOLLAS, Sc.D., F.R.S., F.G.S., delivered a lecture on Man and the Ice-Age.

He said that, thanks to the researches of General de Lamothe, Prof. Depéret, and Dr. Gignoux, the Quaternary System now takes its place as a marine formation in the stratified series.

Four ancient coast-lines, of remarkably constant height, have been traced around the Mediterranean Sea and along the western shores of the North Atlantic Ocean. These, with their associated sedimentary deposits, form the successive stages of the Quaternary System: namely, the Sicilian (coast-line about 100 metres); the Milazzian (coast-line about 60 m.); the Tyrrhenian (coast-line about 30 m.); and the Monastirian (coast-line about 20 m.).

The Sicilian deposits rest unconformably upon the Calabrian

(Upper Pliocene), and in their lower layers contain a characteristic cold fauna. The fauna of the Milazzian is warm-temperate, of the Tyrrhenian and Monastirian still warmer, for they contain numerous species of mollusca which now live off the coast of Senegal and the Canary Islands.

The three lower coast-lines correspond with the three lower river-terraces of the Isser (Algeria), the Rhône, and the Somme. Hence it may be inferred that the position of the river-terraces has been determined by the height of the sea-level.

The lower gravels of the three lower terraces of the Somme all contain a warm fauna, *Elephas antiquus* and *Hippopotamus*, and thus (like the corresponding marine sediments) testify to a warm climate. The climate of the Quaternary age was, on the whole, warm-temperate or genial, but interrupted by comparatively short glacial intervals.

The outermost moraine (Mindel) of the Rhône Glacier is associated with the Milazzian terrace, the intermediate moraine with the Tyrrhenian, and the innermost moraine (Würm) with the Monastirian: except for their serial order, these associations are (in a sense) accidental.

It is now possible to assign the Palæolithic stages of human industry to their place in the Quaternary System: thus the 'Strepyan' or pre-Chellean is Milazzian in age; the typical Chellean—Tyrrhenian; the evolved Chellean, Acheulean, and Lower Mousterian—early Monastirian; and the Upper Mousterian, Aurignacian, Solutrian, and Magdalenian—later Monastirian.

The coast-lines of the Northern Hemisphere appear to have their counterparts in the Southern Hemisphere, and the researches of Dr. T. O. Bosworth in Peru and Prof. G. A. F. Molengraaff in the East Indies have revealed extensive marine Quaternary deposits and successive movements of the sea-level.

The Quaternary movements are probably due to a general deformation of the globe, involving eustatic changes in the level of the sea.

February 7th, 1923.—Prof. A. C. Seward, Sc.D., F.R.S.,  
President, in the Chair.

Mr. G. VIBERT DOUGLAS delivered a lecture on the Geological Results of the Shackleton-Rowett (*Quest*) Expedition. The Lecturer said that St. Vincent and St. Paul's Rocks were examined on the way out, but the more detailed work commenced in South Georgia. This island lies 900 miles east of Cape Horn and is 100 miles long by 20 miles in width. Its topographical features are those of an upland dissected by glacial action. The glaciers in general show signs of withdrawal. Geologically,

the island is composed of sedimentary rocks and, at the south-eastern end, igneous rocks. These have been classified by Mr. G. W. Tyrrell as follows :

Sedimentary Rocks...	(1) Mudstones, shale, slate, phyllite.
	(2) Quartzite, greywacké.
	(3) Calcareous rocks.
	(4) Tufaceous rocks.
Igneous Rocks .....	(1) Gabbros and peridotite.
	(2) Dioritic and granitic rocks.
	(3) Dolerites and basalts.
	(4) Spilitic lavas and epidiosites.

The question as to whether the sediments represent one continuous period of deposition is open to dispute. The Lecturer thought that there were two distinct periods, divided by an unconformity. Definite fossil evidence is difficult to obtain, but *Araucarioxylon* has been identified by Prof. W. T. Gordon, which would point to an age not older than Lower Carboniferous. This fossil came from the Bay of Isles, and was found in what the Lecturer believes to be the younger series. The rocks all show signs of metamorphism, and the strike of the folds and lamellæ of the phyllites would point to the fact that the pressure came either from the south-south-west or from the north-north-east. Considerable faulting was observed, both normal and reversed.

The igneous complex east of Cooper Bay can be differentiated into two separate areas : (1) north of Drygalski Fjord, and (2) at Larsen Harbour. In the former area quartz-diorite, peridotite, aplite, and syenitic lamprophyre with basement gabbro occur ; in the latter area were found spilitic lavas (containing much epidote) and basement gabbro. The general types are not Andean.

Elephant Island is situated in the Powell Group of the South Shetlands. Topographically, it is an ice-covered plateau rising to about 1200 or 1500 feet above sea-level. The rocks on the northern shore have been described by Mr. Wordie as contorted phyllites. The Lecturer's observations at Minstrel Bay on the western coast showed that the rocks there were similar. At Cape Lookout, on the south side of the island, a metamorphic series was encountered : this, according to Dr. C. E. Tilley, consists of amphibolite, garnet-albite-schist, quartz-hornblende-epidote-schist, and banded sandy limestone.

Observations from the ship were made of the volcanic island of Zavodovski, in the South Sandwich Group. The Tristan da Cunha Group in the Southern Atlantic, 1500 miles west of the Cape of Good Hope, was also visited. The islands are of volcanic origin. Particular attention was paid to the existence of Middle Island.

Gough Island lies more than 200 miles south of the Tristan da Cunha Group, and is 8 miles long by 3 miles in width. It is a monoclinical block, with dip-slopes to the west and escarpments to

the east. The lavas forming these features are basaltic, and intrusive into these lavas is a trachytic stock. Following this intrusion, the basalts were cut by a series of doleritic dykes. In general, it may be said that Gough Island presents many features similar to those that characterize the islands of Ascension and St. Helena.

February 16th, 1923.—Prof. A. C. Seward, Sc.D., F.R.S.,  
President, in the Chair.

The President delivered his Anniversary Address on The Earlier Records of Plant-Life. Attention was drawn to the danger of excessive absorption in descriptive work, leading to insufficient consideration of such conclusions of general geological interest as can be drawn from the accumulated data. Reference was made to the views of Dr. Church on the origin of life in the waters of a primeval world-ocean, and on the origin of terrestrial vegetation from highly-organized Algæ transferred by emergence of portions of the Earth's crust above the surface of the water from an existence on the ocean-floor to life on land. It was suggested that the vegetation of the land may have received additions from upraised portions of the crust at more than one epoch in the history of the Earth. The course of evolution could probably be more correctly illustrated by the conception of separate lines of development, than by that of a branching tree implying the common origin of the main groups of plants. The unfolding of plant-life must be considered in relation to the changing geological background. The climatic and physical conditions of the Pre-Cambrian Era were briefly considered, and various kinds of indirect evidence of the existence of plant-life were critically examined: reference was made to graphite, supposed algal remains in association with oolitic structure, *Cryptozoon*, and the structures described by Dr. C. D. Walcott as Algæ or as the result of algal agency. Attention was called to the importance of carefully investigating diffusion-phenomena, as illustrated by the so-called Liesegang figures, as a possible explanation of the origin of some of the structures which are usually attributed to organic agency. We have no knowledge of any Pre-Cambrian land-flora. Palaeobotanical records from Cambrian, Ordovician, and Silurian strata were briefly summarized, including some account of *Girardinella*, *Eophyton*, *Solenopora*, *Nematophycus*, *Pachytheca*, and *Parka*. Reasons were given for assigning some of the Cambrian Algæ described by Dr. Walcott to the Cyanophyceæ, especially *Marpolia spissa*.

In the second part of the Address, the older Devonian floras were reviewed, and some of the more characteristic genera described, special attention being directed to the petrified plants from the Rhynie chert-bed, discovered by Dr. W. Mackie, and described in detail by Dr. R. Kidston and Prof. W. H. Lang. Reference

was made to the differences between the older Devonian floras and those of Upper Devonian age. The question of the common origin of the phyla of Lycopods and Ferns was considered, and preference was expressed for the view which regards them as independently-evolved groups. In conclusion, the wide geographical range of *Archæopteris* was emphasized, and reference was made to the difficult problems raised by the occurrence of Upper Devonian floras well within the Arctic circle, at least equal (in the variety of the plants and in the vigorous development of the vegetation) to the more southern floras of Ireland, Belgium, and other regions.

February 28th, 1923.—Prof. A. C. Seward, Sc.D., F.R.S., President and, afterwards, Prof. W. W. Watts, Sc.D., F.R.S., Vice-President, in the Chair.

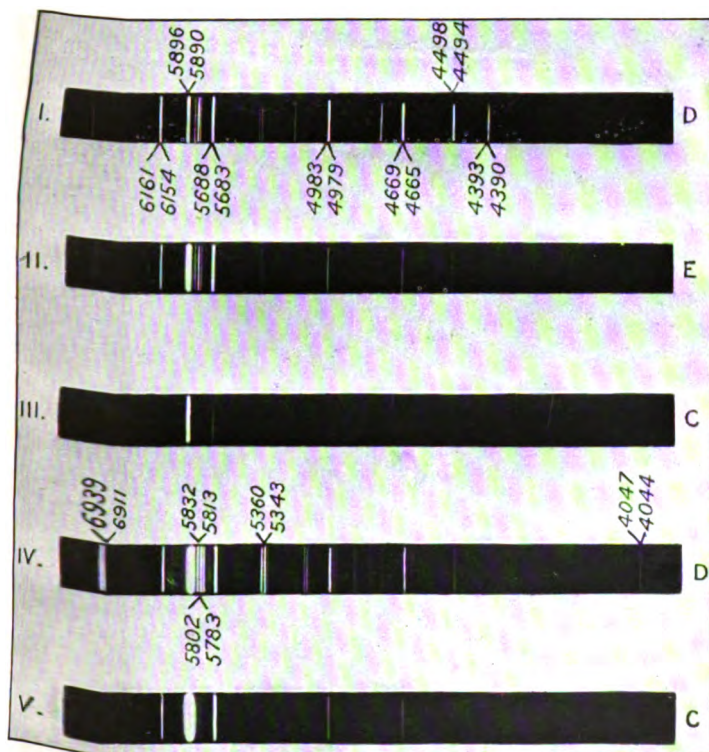
The following communications were read:—

1. 'The Late Glacial Stage of the Lea Valley (Third Report).' By Samuel Hazzledine Warren, F.G.S.

Since the publication of the previous papers on the subject, one new section of the same series of deposits has been found. This was in a different situation from the others, as it occurred at the level of, and in the area occupied by, the Middle or Taplow Terrace, whereas all the other sections were in the Low Terrace. It consisted of a bed of seed-bearing clay, in the middle of an old gravel-pit, partly built over, and consequently its precise stratigraphical relations to the Taplow gravel were not discoverable. The Taplow deposits yield a fairly temperate fauna and flora, and it is therefore concluded that the Arctic deposit cannot be of Taplow date. The site is close to the head of a small streamlet, and it is assumed, although it cannot be proved, that the Arctic plant-bed is of Low-Terrace or Ponders-End date, and that it represents the silting of a stream which flowed across the Taplow Terrace.

The paper is accompanied by a report on the Arctic flora by Mrs. E. M. Reid & Miss M. E. J. Chandler, in which some 48 species of flowering plants are recorded, and the conclusion is reached that there is nothing to distinguish the flora from that of the previously-described localities of the Lea Valley.

2. 'The *Elephas-antiquus* Bed of Clacton-on-Sea (Essex), and its Flora and Fauna.' By Samuel Hazzledine Warren, F.G.S.



I., II., III. Current 5.1 amps.

IV., V. Current 2.0 amps.

D, E, C refer to fig. 1 and indicate where the spectrograms were photographed.

24







FIG. 1.

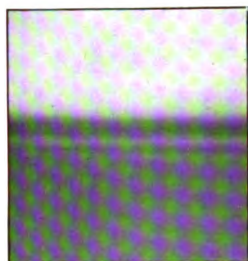


FIG. 2.

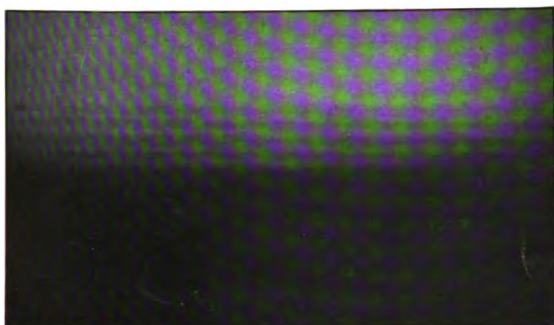
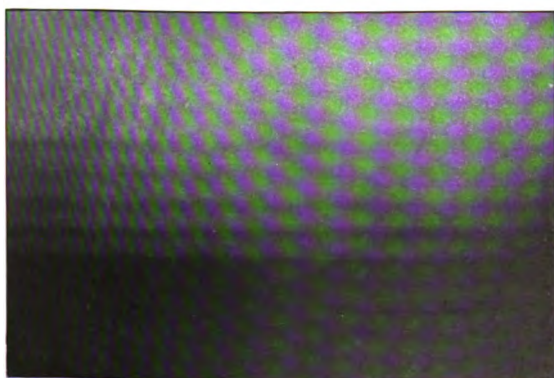


FIG. 3.





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[SIXTH SERIES.]

AUGUST 1923.

**XXIV.** *The Electrification produced by the Pulverization of Aqueous Solutions.* By Prof. J. J. NOLAN, M.A., D.Sc., and Rev. H. V. GILL, S.J., M.A., M.Sc., University College, Dublin\*.

**I**N a previous paper† one of the present writers and another have examined the electric charges produced when water of different degrees of purity is broken up in contact with the air. It was found that the purity of the water was specially important when the degree of breaking-up was small, the purer water yielding the higher charges. When the water was broken into very fine drops, this difference tended to disappear, and it seemed possible that if a sufficient degree of pulverization could be attained, all samples of water would give identical charges. It was also found that as the purity increased, the water was more easily broken into small drops. Considered in connexion with Simpson's theory of thunderstorm electricity, the magnitudes of charge observed showed that if a moderate degree of purity were attributed to the rain-drops in a thunderstorm, the breaking of the drops in the manner supposed by Simpson would produce sufficient separation of electricity to account for the observed effects.

In the work referred to, the purity of the water was varied

\* Communicated by the Authors.

† J. J. Nolan and J. Enright, Sci. Proc. Roy. Dublin Soc. xviii. p. 1 (1922).



by mixing distilled water with tap-water in various proportions. It is important to put the matter on a more definite footing, and to ascertain to what extent the charge is affected by the substances ordinarily present in rain, in the concentrations at which they usually occur. We shall then be in a better position to form an opinion as to how far the results on distilled water are applicable to the breaking up of rain-drops in the atmosphere. The investigation of this point had led to a wider investigation of the effect of dissolved substances in general. Another obvious extension of the work is the examination of water of a still higher degree of purity. The distilled water available for this and the previous work had a specific conductivity as high as  $2.4 \times 10^{-6} \text{ ohm}^{-1}$ . As water of conductivity  $\cdot 1$  to  $2 \times 10^{-6}$  can be prepared without much difficulty, it is clear that there is a considerable range available for investigation. Work on the latter point is now proceeding; the present paper deals with the effect of the ordinary impurities in rain, and then with the effect of dissolved substances in general.

#### *General Experimental Method.*

Experiments on the electric charges produced by breaking up water solutions have been carried out by many observers, especially by Lenard\*, Sir J. J. Thomson†, J. J. Rey‡, and Christiansen§. In almost all cases the breaking up of the liquid was produced by allowing drops to splash against an obstacle. It is not to be expected perhaps that the spraying method used by us should give the same results as the method of splashing, although previous work|| has shown that, in the case of pure water at least, the charge on the water, considered as a function of the new area of surface produced, was the same whether the water was sprayed or broken by falling into an air stream. But, in fact, our results for solutions exhibit considerable differences from those obtained by the splashing method. The method of spraying has the advantage that the degree of breaking up of the liquid is easily controlled and measured. The breaking up can also be carried to a far higher degree, if necessary, than is possible with the other method.

\* P. Lenard, Wied. *Ann.* xlv. p. 584 (1892).

† J. J. Thomson, *Phil. Mag.* xxxvii. p. 341 (1894).

‡ J. J. Rey, *L'ionisation de l'air par les chutes d'eau*. Gauthier-Villars, 1912.

§ Christiansen, *Ann. der Physik*, xl. pp. 107, 233 (1913), clxx. pp. 95, 280 (1919).

|| J. J. Nolan, *Proc. Roy. Soc. A.* xc. (1914).

The method of working is given in some detail in the previous paper\*. The liquid is sprayed in a horizontal direction from a metal sprayer driven by air under pressure. The drops fall into an insulated metal tray. This, together with the sprayer itself, which is also insulated, is connected to a Doležalék electrometer which measures the charge. The electrometer therefore records the charge on the water due to the electric separation at the water-air surface, the charge of the opposite sign being carried off in the air as an excess of ions of one sign. The method of measuring the size of the drops corresponding to each pressure on the sprayer and of computing the corresponding new area of liquid surface produced need not be repeated here.

## PART I.

### *Effect of Substances occurring in Rain.*

In examining solutions of different substances there are two lines of procedure open to us: we can keep the concentration of the solution constant and examine the charge corresponding to different degrees of pulverization, or we can drive the sprayer at a steady pressure and examine the effect of solutions of different strengths. The latter is the method of most interest, especially in the present case. The degree of breaking-up likely to be experienced by rain-drops in nature is even smaller than the smallest produced by our sprayer. Hence we can best examine the effect of the different possible impurities by working at a steady low pressure of the sprayer.

The substances most likely to be present in rain in the free atmosphere are nitrates and nitrites, sodium chloride from evaporated sea spray, hydrogen peroxide and dissolved gases such as ammonia, carbon dioxide, oxygen, and nitrogen. It may be stated at once that, judging from their effect when added to distilled water, these substances, with the single exception of sodium chloride, will not seriously affect the charge developed when a rain-drop is broken. In illustration of this we quote the results obtained when solutions of nitric acid, ammonia, and sodium chloride of various strengths are sprayed. In each case the solutions were sprayed into drops of an average radius of  $7.5 \times 10^{-3}$  cm. The charges per c.c., which are all positive, are given in arbitrary units, the value for distilled water being taken as 100.

\* J. J. Nolan and J. Enright, *loc. cit.*



Standard solution of  $\text{HNO}_3$  ..... 94.5 milligrams per litre.

" " "  $\text{NH}_3$  ..... 15.4 " " "

" " "  $\text{NaCl}$  ..... 40.0 " " "

Positive charge—Distilled water 100.

Strength of Solution.	$\text{HNO}_3$ .	$\text{NH}_3$ .	$\text{NaCl}$ .
2 per cent. of standard .....	82	89	95
5 " " " .....	53	83	86
10 " " " .....	22	74	66
20 " " " .....	14	57	57
30 " " " .....	...	47	47
50 " " " .....	10	45	38
100 " " " .....	7	42	23

The amount of ammonia present in rain collected in country districts may be taken as about .5 mg. per litre. In the tropics the value seems to be higher\*. Similarly for nitric acid, while the values for the tropics are of the order of .2 mg. per litre†, the values found by Boussingault in Alsace and the values found at Rothamsted range from .2 to .4 mg. per litre. Taking the value .5 mg. for ammonia and .3 mg. for nitric acid, we find that these concentrations correspond to about  $\frac{1}{3}$  per cent. of our standard solution in each case. The observations show that ammonia and nitric acid in such quantities would produce no appreciable effect on the charge produced by breaking drops. Even in the concentrations reported from the tropics, these substances, while producing a noticeable effect, would not seriously interfere with the phenomenon. It is otherwise however in the case of sodium chloride. The concentration of this substance in rain varies very widely, depending upon the distance from the sea-shore. McAdie‡ quotes the following values: England (mean) 2.2 mg. per litre. Rothamsted 2.01 mg., Nantes 14 mg., and Troy, New York, 2.7 mg. It would appear that in places remote from the sea shore the concentration can sink below 1 mg. per litre. This would correspond roughly to 2 per cent. of our standard solution of  $\text{NaCl}$ , and, as will be seen, the corresponding reduction in the charge on the water is only 5 per cent. The mean concentration for England would produce a reduction of nearly 20 per cent. in the values for distilled water, while the figure quoted for Nantes, which is no doubt exceeded at many sea-coast stations, would reduce the charging to

\* Marcato & Muntz, *C. R.* cxiv. p. 184 (1892).

† Marcato & Muntz, *C. R.* cxviii. p. 1062 (1889).

‡ McAdie, 'Principles of Aerography,' p. 164. Harrap, 1917.

45 per cent. of the value found with pure water. It is clear then, that in many cases the NaCl content of the rain-water is important, and that while in inland regions the charge developed when a rain-drop is broken will have very nearly the full value, in sea-coast regions this may be reduced to a half or a third.

*Effect of Nitrites,  $H_2O_2$ , and Atmospheric Gases.*

The conclusions reached for nitric acid and ammonia hold for the remaining substances. Nitrites and carbon dioxide in the concentrations in which they occur in rain do not seriously affect the charge given by distilled water. We have also tested air-free water and water saturated with air against ordinary distilled water. We were unable to find any consistent difference. Hydrogen peroxide in the quantity in which it occurs in rain (up to 1 mg. per litre\*) does not produce any noticeable effect.

*Inhibition of Thunderstorms.*

While it is clear that sodium chloride is the only substance occurring naturally in rain that is likely to seriously diminish the charge produced by a breaking drop, it is of interest to inquire what concentrations of some other substances would be required to produce this effect. Some experiments made with ammonia showed that the charging was reduced to 1 per cent. of the value for pure water with a solution containing about .5 gramme  $NH_3$  per litre. If Simpson's theory of thunderstorms is correct, it would seem that if ammonia could be introduced into the thunder-cloud in sufficient quantity to form with the rain-drops a solution of this strength (or even  $\frac{1}{10}$  of this strength) the development of a thunderstorm would be seriously impeded. This is an experiment which is perhaps within the bounds of possibility.

It would also appear that in view of the unusual quantities of inorganic matter in the air over large industrial centres, the frequency and severity of thunderstorms should be somewhat less in these regions. We are not in the possession of any records by which this possibility could be tested.

*Tests on Rain-Water.*

The inquiry which we are carrying out could be made in another fashion—that is, by making the actual tests on rain-water. The rain-water should be collected in districts

\* Schöne, *Berichte*, 1878, p. 482.

remote from towns, in order that the risk of artificial contamination should be as low as possible. The manner of collection and transport should be devised so as to preserve the water as closely as possible in its natural state. We have endeavoured to secure some samples in this way, but the conditions prevailing recently in the districts most suitable for the collection of pure rain-water have not been favourable. Some results may, however, be quoted. A sample collected in Dublin and visibly contaminated with soot gave 35 per cent. of the effect of distilled water. A sample collected near Carnsore Point, co. Wexford (28th Feb., 1923, wind S.W.), gave 40 per cent. of the effect of distilled water. This sample probably contained a good deal of sodium chloride.

We hope to continue these tests at a later date. But even without the extra information which they would yield, our conclusions are fairly clear. Except in the neighbourhood of the sea, the rain-drops may be expected to give nearly the same electrical effects as the distilled water of our experiments. The conclusions of the former paper may therefore be reaffirmed. It was there shown that a rain-drop of diameter 4 mm. breaking in a natural fashion would acquire a positive charge somewhat greater than  $\cdot 2$  electrostatic unit per c.c. Taking into consideration the tendency for evaporation to further concentrate the charge, we consider that the breaking of the drops in the manner supposed by Simpson can yield sufficient electric charge to account for the observed phenomena of the thunderstorm.

## PART II.

### *Investigation of the Effect in general.*

#### *Inorganic Salts—Sodium Chloride.*

While this research was intended originally as an investigation into the physical basis of Simpson's theory, it was soon found desirable to extend its scope. We had noticed that all inorganic substances which we tested behaved in very much the same way. With increasing concentration they gradually diminished, but did not (within the limits of concentration used by us) reverse or annul the positive charge due to pure water. We wished to observe the behaviour of a substance which would produce a reversal of sign. If there is anything which has been regarded as well established about electrification by the breaking of water, it is that sodium chloride in increasing quantities first diminishes and then

reverses the positive charge obtained with pure water. This result was found by Lenard\* in his pioneer work on the subject. He found that the solution began to give a negative charge at a concentration of less than .01 per cent. NaCl, and that the maximum negative charge was given by a solution of 6.5 per cent. J. J. Rey† found that the charge changed sign at a concentration of about  $\frac{1}{2}$  gramme of NaCl per litre, and that it reached a maximum negative value at about 10 grammes per litre.

In an extended series of tests made by our method, using solutions of strengths varying from 100 grammes NaCl per litre down to the very dilute solutions mentioned in the first part of this paper, we were unable to detect any indication of negative charging. This was the case not only with sodium chloride but with all inorganic salts which we tested. For example, chromium trioxide and potassium permanganate, which at concentrations of .0064 and .25 grammes per litre respectively gave negative charges in Sir J. J. Thomson's work, were with us always positive. In all cases increasing concentration diminished the positive effect due to pure water, but in no case were we able to obtain a reversal of sign. We did not test all the salts mentioned by other writers, as in order to clear up the discrepancy, we thought it best to confine our attention to the outstanding case of sodium chloride.

It was natural to infer that the real difference between the spraying and the splashing methods was a difference in the degree of pulverization produced. The sprayer breaks up the water very effectively, and the charges produced are very much higher than those obtained on water which has splashed. We might assume then, that the failure to obtain negative charging with salt solutions was in some way due to a too drastic pulverization of the liquid. The negative charge might be expected to appear if the pulverization were reduced to something corresponding to that produced by splashing. The extent to which the liquid is broken up can be controlled by varying the air-pressure at which the sprayer is driven. This necessitates the consideration at this stage of the relation between these two quantities, air-pressure and pulverization.

This point has not arisen before in this paper, as up to the present we have been comparing different solutions which were all sprayed at the same pressure and broken into drops

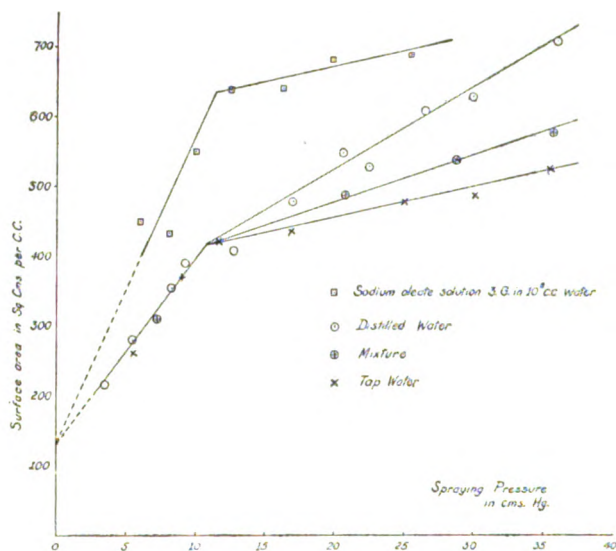
\* Lenard, *loc. cit.*

† Rey, *loc. cit.*



of the same size. The graphs of fig. 1 (which is in the main taken from a previous paper\*) show the efficiency of the sprayer at different pressures. The area of liquid surface per c.c. of water sprayed (or what is roughly the same thing  $\frac{3}{r}$ ,  $r$  being the mean radius of the drops) is plotted against the pressure on the sprayer. The lower set of graphs deal with distilled water, tap-water, and a mixture of the two.

Fig. 1.



It is clear that the three samples of water behave as one until a pressure of 11 cm. Hg. is reached. Then they separate, and the pure water is, at a given pressure, broken into smaller drops than the less pure samples. We have not gone through the rather laborious process of taking observations on the sizes of drops at various pressures for any of the sodium chloride solutions. We have assumed that the dilute solutions would not differ very much in their behaviour, at pressures below 11 cm. Hg., from the three water samples.

If, as already suggested, the non-appearance of the negative charge for salt solutions is due to excessive pulverization, we

\* Nolan & Enright, *loc. cit.* In the graphs given in the previous paper some points were accidentally omitted by the draughtsman. They have been restored here.

might expect to detect the change of sign by working from 10 cm. Hg (the normal spraying pressure) downwards. We have therefore on many occasions tested salt solutions at every available spraying pressure. At the lowest pressure at which the sprayer would function we obtained no indication of negative charge. Solutions of a strength which according to Lenard and Rey should have been definitely negative were with us definitely positive, the positive charge increasing with increasing pressure on the sprayer.

It was not until after the completion of most of the work described subsequently in this paper, that we finally obtained a negative charge from salt solutions. The result was ultimately arrived at (contrary to our expectations) by testing strong solutions at *high* degrees of pulverization. We give some results obtained for a solution of 30 grammes NaCl per litre and also for sea-water. The values for the latter are the means of observations on three samples collected at Howth, Blackrock, and Dalkey.

	PRESSURE.			
	10 cm.	20 cm.	30 cm.	40 cm.
NaCl solution 30 g./litre .....	+14	+4	-32	-76
Sea-water .....	+23	+9	-26	-70

The numbers given represent in arbitrary units the charge produced per second. In order to compare them with one another, one must not only take account of the differing degrees of pulverization, but of the increasing quantity of water driven through the sprayer at the higher pressures. It is enough, however, at present to see that the negative charge has made its appearance at the high degrees of pulverization. In order to give an idea of relative magnitudes of charge, it may be stated that on the scale of the figures quoted, the charging of distilled water at 10 cm. pressure would be represented by about 2000, and at 40 cm. pressure by about 15,000. It may also be stated that while the three samples of sea-water yielded results in very good agreement, solutions of NaCl of apparently uniform concentration gave results which fluctuated very considerably. The values given above represent a set of observations on one particular day. It is of little advantage to give a mean value of many observations, as the fluctuations were very irregular. The further consideration of the appearance of the negative charge in these cases can with advantage be deferred to a later stage in this paper.

The general conclusions reached in this section may be re-stated. Inorganic salts (as far as our examination goes) diminish the positive charging due to distilled water, but do not reverse it except (in the case of NaCl, at least) when strong solutions are subjected to a high degree of pulverization. The negative charging then produced is relatively very small and irregular.

#### *Non-Electrolytes.*

We have carried out tests on a number of substances which do not dissociate in aqueous solution. These included glucose, maltose, lactose, and urea. Solutions of different strengths were examined. We could find no certain difference between these solutions and distilled water. Certain effects must be guarded against. It is clear that if the substance under test is impure, the impurity may be present in sufficient quantity in a strong solution to seriously affect the charge. A strong solution of maltose which readily frothed on being shaken up (in itself a sign of impurity) gave a charge much less than that of distilled water. This we explained in the fashion just mentioned. On the general evidence of the other substances, we concluded that non-electrolytes are ineffective in interfering with the normal charging produced when pure water is broken up.

#### *Very Active Substances.*

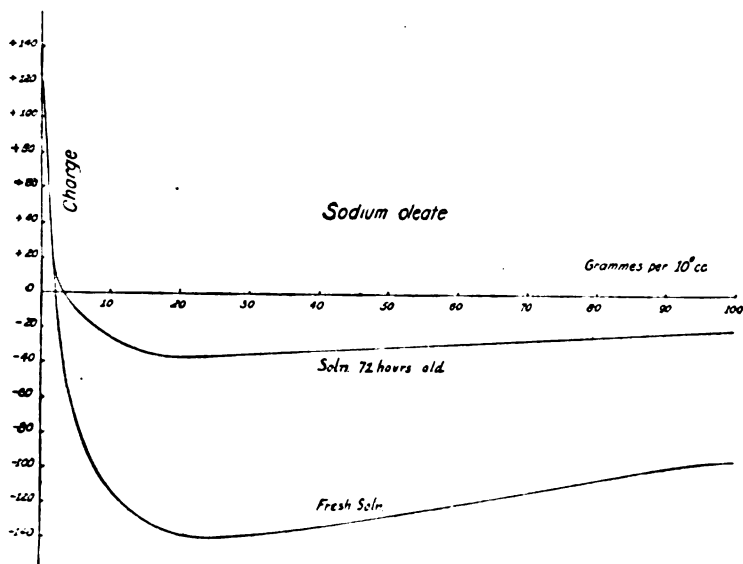
We have next to consider a group of substances which affect the electric charge developed by water very strongly. The effects produced by some substances of this class have been examined by Sir J. J. Thomson and others. We first noticed this effect with sodium oleate. This substance when present in water, even in very small quantities, readily reverses the charge. The curves in fig. 2 show how the charge produced depends upon the degree of concentration when the sprayer is driven at our standard pressure (10 cm. Hg). The positive charge on distilled water is reduced to zero by the addition of between 2 and 2.5 grammes of sodium oleate per  $10^6$  c.c. At higher concentrations the charge is negative, a maximum negative value being reached at about 20 grammes per  $10^6$  c.c. When relatively very high concentrations are reached the charge changes sign once more. The positive charge appears at a concentration a little less than 5 g. per litre.

To show the sharpness of the first reversal of sign, we quote the following observations :—

	Charge.
Distilled water.....	+120
1 g. Sodium oleate per 10 <sup>6</sup> c.c. water .....	+ 71.5
2 g. " " " " " " .....	+ 19.5
2.5 g. " " " " " " .....	- 16
3 g. " " " " " " .....	- 41.

The activity of the sodium oleate solutions changes with time. The numbers given above refer to freshly prepared solutions. A curve is given (fig. 2) for solutions which

Fig. 2.



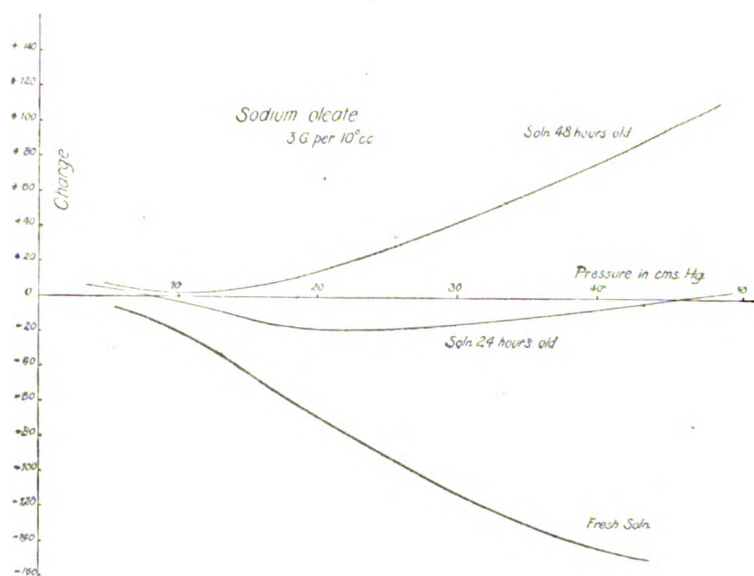
were three days old. The negative charging is much less marked. It was noticed that while the more dilute and the stronger of these solutions were quite clear, those of middle strengths showed some opacity. All solutions were quite transparent when first prepared. On testing, it was found that the more opaque solutions corresponded roughly with those giving the greater negative charges. This effect would seem to be connected with the periodic opacity of colloids investigated by Holker\*.

\* Holker, Proc. Roy. Soc. A. cii. p. 710 (1923).



The tests described were made with the sprayer working at the usual pressure. We also investigated the effect of varying the degree of pulverization, keeping the strength of the solution constant. The result of a test is shown in fig. 3. A solution of 3 grammes sodium oleate per  $10^6$  c.c. when freshly prepared gives a negative charge, the charge increasing with the degree of pulverization. When one day old it gives a small positive charge at low pressure, changing over to a weak negative at high pressure and back again to

Fig. 3.



positive at still higher pressures. The solution when two days old is positive for all degrees of pulverization.

For the same solution we also investigated the relation between the pressure on the sprayer and the degree of pulverization produced. The relation is shown graphically in fig. 1. We were surprised to find that at all pressures the pulverization produced was much greater than in the case of distilled water. There is no doubt about this result, as a set of observations was made alternately with the solution and with distilled water. The values found for the latter were in good agreement with the values found previously (Nolan & Enright). Observations were made on

solutions of different ages ; all gave approximately the same results\*.

The pulverizing action of the sprayer changes at a pressure of about 11 cm. Hg, where all the graphs bend over. The pulverization produced in the two stages seems to depend on two different properties of the liquid. Whatever property is concerned in the first stage does not seem to be affected by the addition of tap-water to distilled water ; the three lower graphs have that part in common. The property concerned in the second stage is affected by the impurity of tap-water, and the impurity operates to reduce the pulverization. On the other hand, in the case of the sodium oleate solution, all the ordinates of the first part of the graph are increased by over 40 per cent.†. The second part is approximately parallel to the corresponding part of the graph for tap-water. Thus the sodium oleate, while modifying in the same fashion and to about the same degree as the impurities of tap-water the property of pure water involved in the second stage, operates in a novel and very marked fashion to increase the pulverization in the first stage. We are inclined to associate the effect in the first stage with the dynamic surface tension. Freundlich‡, following Lord Rayleigh§, finds for the dynamic surface tension by the jet method the value 79 dynes/cm. for solutions of sodium oleate of concentrations .025 and .25 per cent., while the value found for pure water is 75.

*Methylene Blue, Congo Red, Methyl Orange, and Sodium Glycocholate.*

Curves for methylene blue and congo red are given in fig. 4. Methylene blue produces a remarkable effect, .5 gramme per  $10^6$  c.c. of water being sufficient to reduce the positive charge to zero. The negative charge has a sharp maximum at 2.5 g. per  $10^6$  c.c., and the charge once more becomes positive at about 11 g. per  $10^6$  c.c. In addition to the observations which are plotted and which were taken at our standard spraying pressure (10 cm. Hg), we

\* For observations on sodium oleate and for checking the previous results on distilled water, we are much indebted to Mr. A Fynn, S.J.

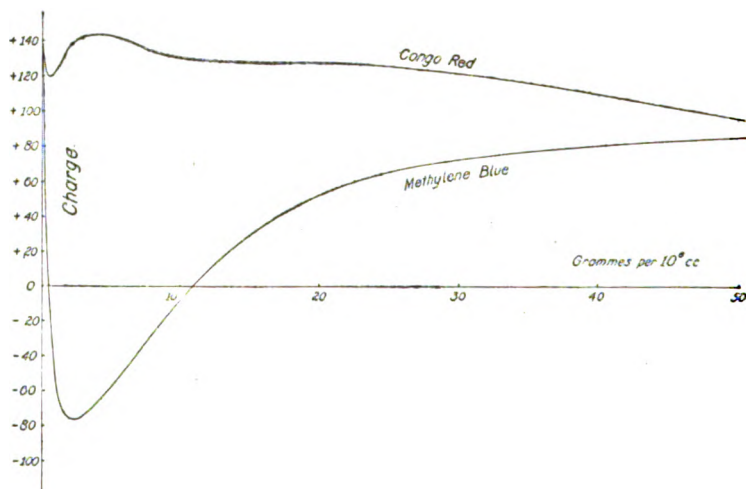
† By more than 60 per cent. if we assume that the intersection of the graph with the axis gives the true zero of surface. See Nolan & Enright, *loc. cit.* p. 8.

‡ Freundlich, *Kolloidchemie*, p. 56 (1909).

§ Rayleigh, *Proc. Roy. Soc. A.* xlvii. p. 281 (1890).

also took observations at double that pressure. The reversal of sign now occurred at some concentrations below  $\cdot 4$  g. per  $10^6$  c.c. The maximum negative charge occurred at exactly the same concentration as before, and the second reversal took place at  $13$  g./ $10^6$  c.c. instead of  $11$  g./ $10^6$  c.c. All readings were much increased, the maximum negative reading being four times as great as before. With congo red the effects are not so striking. At very small concentrations there appears to be a sharp dip in the values for charge. Then follows a rise to a value slightly greater than that for pure water, and subsequently a slow falling-off.

Fig. 4.



In fig. 5 are shown the results of measurements on methyl orange. Here the effects are well defined. There is first a 33 per cent. rise from the value for water to a sharply-defined positive maximum at  $\cdot 75$  g./ $10^6$  c.c. The positive charge is reversed at  $5\cdot 5$  g./ $10^6$  c.c., and a negative maximum is reached in the neighbourhood of  $24$  g./ $10^6$  c.c. The negative charge decreases, and the solution goes positive once more at a concentration of about  $\cdot 8$  g. per litre.

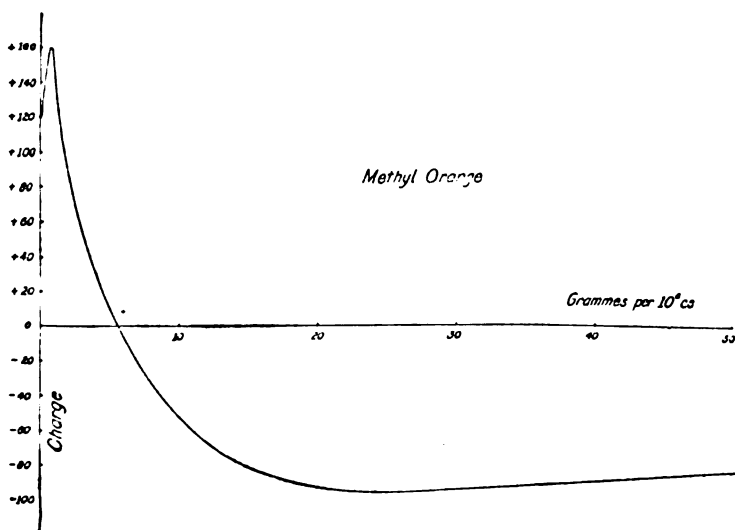
The behaviour of these four substances—sodium oleate, methylene blue, congo red, and methyl orange—differs in a very remarkable way from that of the ordinary inorganic salts and of non-electrolytes. In a research on adsorption,

Lewis\* has found a group of substances which depart widely from the adsorption law founded on thermodynamic reasoning by Willard Gibbs. The expression arrived at by Gibbs is

$$\gamma = - \frac{c}{RT} \cdot \frac{d\sigma}{dc},$$

where  $\gamma$  is the excess surface concentration of the solute,  $c$  the bulk concentration, and  $\sigma$  the interfacial tension. Lewis found that this law held fairly well for ordinary inorganic

Fig. 5.



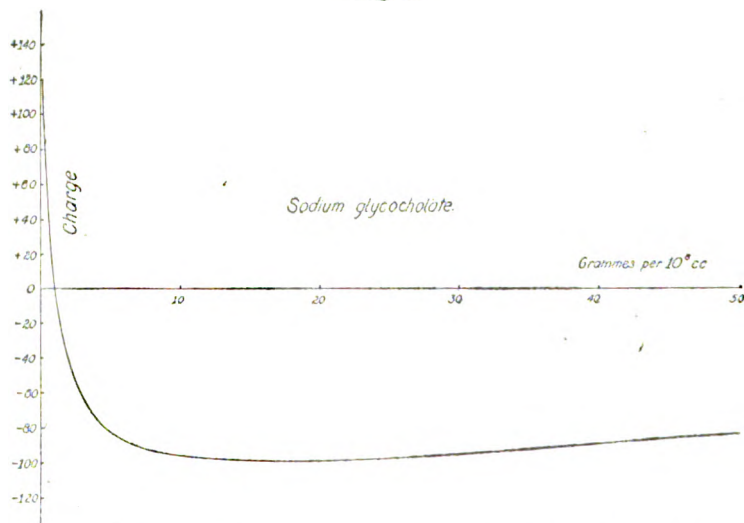
salts and for caffeine, a non-electrolyte ; but he noted very wide departures from it in the case of four substances : sodium glycocholate congo red, methyl orange, and sodium oleate. These substances appeared to be present in the surface layers in concentrations of the order 100 times as great as would be expected from the variation of surface tension with concentration, assuming that Gibbs's law holds. As three of these substances are found by us to be equally remarkable in their electric effects in very dilute solution, we decided to test the fourth. . A quantity of sodium glycocholate was obtained (British Drug Houses) and tested.

\* W. McC. Lewis, Phil. Mag. xv. p. 499 (1908), & xvii. p. 406 (1909).

The result is shown in fig. 6. The curve resembles that obtained for sodium oleate. The positive charge is reversed at a concentration of about 1 g./10<sup>6</sup> c.c. and attains a maximum negative value at about 15 or 20 g./10<sup>6</sup> c.c. It changes sign again (not shown on curve) at 340 g./10<sup>6</sup> c.c. and goes increasingly positive, the positive charge being, at a concentration of 1 g. per 100 c.c., 25 per cent. higher than that of pure water.

In view of these results, there can hardly be any doubt that the abnormal electrical effects obtained by us are

Fig. 6.



connected with the abnormal adsorptions found by Lewis. Lewis speculates as to the existence of an electrical effect of some kind in the surface layer, but rejects this explanation of the anomalous adsorption, as he considers that it should also manifest itself in the case of other electrolytes, such as the ordinary inorganic salts. The experiments just recorded show that the electrical surface conditions in solutions of these substances must be very different indeed from those prevailing in an ordinary electrolyte.

#### *Examination of other Substances.*

Other substances were examined, but the effects were not so marked as in the case of those just dealt with. The results are given briefly below.



*Glycerine.*—The following values were found for solutions of glycerine:—

	Charge.
Distilled water .....	+115
·625 g. glycerine to 100 c.c. water .....	+127
1·25 " " " " .....	+140
2·5 " " " " .....	+155
5·0 " " " " .....	+164
10·0 " " " " .....	+170

*Starch.*—A very weak solution increased the positive charge of water slightly. For concentrations higher than 1 g./litre the charge diminished.

*Eosin.*—The positive charge was reversed at a concentration of 8·5 g./10<sup>5</sup> c.c. With increasing concentration solutions remained negative as far as tested (1 g./litre).

*Fluorescence.*—Positive charge was reversed between ·5 and 1 g./litre.

*Picric Acid.*—Positive charge was reversed at ·25 g./litre. Stronger solutions were very faintly negative.

*Possible Effects of very active Substances occurring as Impurities.*

The effect which such substances as sodium oleate produce when present in minute proportions shows the necessity for strict attention to the purity of all solutions. The impurity may arise in a most unexpected form and in a form not detectable by ordinary chemical methods. For example, on one occasion we found it necessary to filter a solution, and suspicion was aroused as to whether the filtering had not affected the electrical activity. We tested the filter-paper by allowing distilled water to filter through it into our spraying-vessel. We found that the filter-paper reduced the charge on distilled water to 20 per cent. of its original value. This experiment was repeated with several filter-papers, all new and of good grade. The result was the same in each case. Christiansen\* gives an account of experiments with filter-paper and other materials, all tending to show the great effects that may be exercised by minute traces of active substances. We may quote another instance which is very suggestive. After tests on solutions of methyl orange, traces of this substance remained in our spraying-vessel, in spite of repeated washings with distilled water. As a result, solutions of NaCl of about 1–2 g. per litre,

\* Christiansen, *Ann. der Physik*, xl. p. 107 (1913).

which normally gave positive charges when tested in the usual way, were now distinctly negative. It was not until after two days of continued washing of the vessel that the usual positive charge re-appeared. Experiments of this kind show that it is very difficult to determine what is the true effect of any substance in concentrated solution. Thus, if a substance like methylene blue were present as an impurity in sodium chloride to the extent of 1 part in 30,000, it would certainly cause a solution of 30 NaCl per litre, normally positive, to show a strong negative charge, and this negative charge would increase rapidly as the degree of pulverization increased.

Our results suggest that the negative charging in the case of inorganic salts found by most workers, and found by us in the case of NaCl at high degrees of pulverization, is due to the presence of impurities. If this view is adopted, a ready explanation is found of many features of the effect which are otherwise puzzling. Thus, while both Lenard and Rey use the splashing method, the concentration of NaCl solution at which the negative charge appears is .1 g./litre in one case and .5 g./litre in the other. Lenard found the maximum negative charge at 65 g./litre, Rey at 10 g./litre. We do not hold that the non-appearance of the negative charge with salt solutions in our experiments is due to the fact that our solutions are any purer than those used by other workers. But if the impurity present is of the nature of sodium oleate, the adsorption experiments of Lewis show that in a falling drop the impurity will attain to a very high degree of concentration in the surface layer, thus favouring its exerting a maximum effect when the drop splashes. The formation and disruption of surface layers in the sprayer must be a much more rapid process, and the concentration of the solute at any surface momentarily formed is very much less than in the surface of a drop which forms slowly, breaks off, and then falls some distance through air, as in the splashing experiments. On these lines we readily find an explanation of the discrepancies between the results for salt solutions obtained by the two methods. It will be remembered also that both the splashing and the spraying methods give the same results when dealing with pure water\*. In the same way the results of another experiment find explanation. A strong salt solution gives a positive charge when sprayed at our ordinary spraying pressure. If the same solution is exposed in an open vessel to a strong

\* J. J. Nolan, Proc. Roy. Soc. A. vol. xc. (1914).

jet of air, it is found that the liquid begins to assume a charge as soon as the jet is strong enough to bear its surface. But the charge is negative, although the degree of breaking up of the liquid surface is very much less than that produced by the sprayer. On our view, the active impurity is very strongly concentrated in the surface layer, and is exercising its maximum negative effect.

The nature of the charge developed on strong salt solutions tends to support this view. In all our work on weak salt solutions the observations are easily repeatable to a good degree of accuracy. When the routine precautions of washing out the spraying vessel, etc., are attended to, there is never any uncertainty as to the electrical readings. The case is quite different with strong salt solutions, as has been noted earlier in this paper. The following readings, for example, were taken on different days with a solution of NaCl 30 g./litre, the spraying pressure being 40 cm.: -76, -56, -35, +9, +7, -38, -40, -30, -25. In all cases conditions appear to be identical. There was no known contamination, yet we have not only a fluctuation in the value of the negative charge, but a change over to positive on two occasions.

These results are best explained by assuming the existence of an impurity which varies in concentration. We have experimented with solutions of highly purified sodium chloride, but so far without obtaining any satisfactory results. Our experience with filter-paper shows that ordinary chemical standards of purity do not apply here. We are inclined to think that the salt solution itself reacts on the walls of the containing vessels, or on something attached to these walls to form the impurity. It would certainly seem as if strong salt solutions were more sensitive to contamination of the vessel, as in the case of methyl orange referred to already, than distilled water. In our view there is no decisive evidence that a pure solution of an ordinary inorganic substance ever assumes a negative charge when broken up in air.

We do not think it useful, at present, to attempt a theoretical interpretation of these effects. We have good reason for believing that electrolytes alone are active; that ordinary electrolytes act in a simple way to reduce the charging due to pure water; that certain electrolytes, in each of which one of the ions is very complex (in four cases the negative ion, in one the positive ion), produce notable effects accompanied by change of sign in dilute solutions; that these same substances are distinguished by abnormal



adsorption effects. Further experimental work is necessary before we can hope to understand the mechanism of these phenomena.

*Summary.*

PART I.

1. The substances ordinarily present in rain, sodium chloride excepted, will not appreciably diminish the charge produced when a rain-drop is broken in air.

2. The amount of sodium chloride present in rain in maritime districts will produce a considerable reduction.

PART II.

1. Inorganic salts in increasing concentration diminish the positive charge produced when water is broken.

2. Non-electrolytes do not affect the development of charge.

3. A group of substances shown by Lewis to give abnormal adsorption effects have a great influence on the sign and magnitude of the charge at very low concentrations.

4. It is suggested that certain results on inorganic salts obtained by other observers are due to the presence of impurities.

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XXV. *An Investigation of the Angle of Contact between Paraffin Wax and Water.* By R. ABLETT, M.Sc., *George Holt Physics Laboratory, University of Liverpool* \*.

THE primary objects of this research were

- (1) to devise a more accurate method of determining the contact angle ;
- (2) to investigate the differences in the angle of contact
  - (a) when the liquid has previously been in contact with the solid,
  - (b) when there has been no previous contact.

A difference was expected between the angles in cases (2a) and (2b), and it was hoped that this would throw some light on the acknowledged difference in the lengths of the column of liquid in a capillary tube according as there is a rising or a falling meniscus. It was also hoped to throw some light on

\* Communicated by Prof. L. R. Wilberforce, M.A.

the phenomenon of "wetting," which seems to be such an important factor in lubrication and ore concentration by the method of flotation.

The method consists essentially in immersing a cylinder, with its axis horizontal, to such a depth that the free liquid surface is plane right up to the line of contact with the curved surface of the cylinder. It is clear that in such a position the tangent plane to what would under other conditions be the curved portion of the free surface must coincide with the tangent plane to the curved surface of the cylinder at the line of contact. Then if  $h$  be the height of the free liquid surface above the lowest generator of the cylinder, and  $d$  be the diameter of the cylinder, it can easily be shown that  $\cos \theta = \left(2\frac{h}{d} - 1\right)$ , where  $h > \frac{d}{2}$  gives acute angles, and  $h < \frac{d}{2}$  gives obtuse angles.

Since the distinction between a rising and a falling meniscus is primarily that of direction of relative motion of the liquid and solid, the phenomenon can be reproduced by keeping the liquid stationary and imparting motion to the solid. Accordingly an apparatus was devised for rotating the cylinder either clockwise or anti-clockwise about its horizontal axis, the former corresponding to the liquid leaving the solid, *i. e.* to a falling meniscus, and the latter to the liquid encroaching on the solid, *i. e.* to a rising meniscus. It seemed probable that the difference between the angles of contact in the two cases would depend on the relative velocity, so a reduction gear capable of variation was devised.

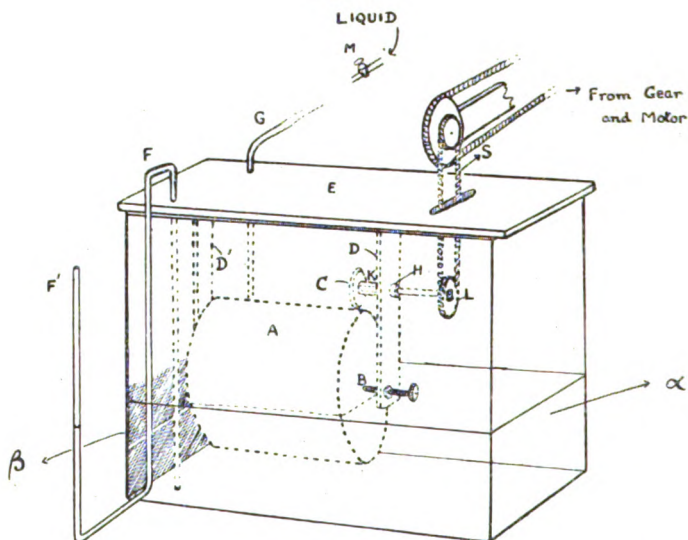
### *Apparatus.*

In the final condition the apparatus is shown in fig. 1. A is a solid glass cylinder about 3 in. diam. and 3 in. long.

It is supported by the conical ends of the steel screws B, B', which fit into small holes, about 1 mm. diam. and 1 mm. deep, at the centre of the end faces of A. The screws B, B' fit into a solid brass support D D', 1 in. by  $\frac{1}{4}$  in., which is screwed on to the under face of the wooden top E. C is a brass wheel with a rubber tyre acting as a friction wheel on the cylinder. The axle of C passes through a brass sleeve K and the support D, and is screwed on to the pulley wheel L. The collar H and the sleeve K limit the lateral movement of C. The wooden top E fits tightly on the top of a rectangular glass tank. The whole is so arranged that the axis of A is horizontal and parallel to the long faces of the tank.

G is a glass tube connected by a flexible rubber tubing to a large aspirator bottle used as a reservoir for the water. The flow of the water is regulated by means of the tap M. The thermometer T gives the temperature of the water to  $0^{\circ}\cdot 1$  C. F F' is a siphon manometer of glass tube about 1 cm. diameter. The motion is supplied by means of a small electric motor, and is varied by means of a band reduction gear assisted by a variable resistance in parallel with the motor.

Fig. 1.



At first great difficulty was experienced in preventing the transmission of vibration through the various belts to the cylinder, and hence to the water surface. As the belt S was the only connecting link between the gear mechanism and the pulley L, rubber bands and rubber cord of various grades were tried, but without success. Finally it was found that by substituting a closely wound helical spring adjusted to a suitable tension, vibration was eliminated, and the power necessary to rotate L and the cylinder A was transmitted. The large box on which the tank stood was supported on three rubber pads to prevent the transmission of vibration from the floor.

#### *Experimental Details.*

The curvature of the water/air surface was tested by using the surface as a mirror to reflect a narrow parallel beam of

light. As in preliminary trials it was found that the angle of contact for paraffin-wax and water was greater than  $90^\circ$ , the under face of the water/air surface was used as a reflector, thus making it possible to test the surface *right up* to the line of contact with the cylindrical surface. (For  $\theta < 90^\circ$ , the upper face of the surface would be better.) The surface was viewed from the right-hand side of the tank ( $\alpha$ ) in fig. 1. The left-hand side ( $\beta$ ) was covered with dull black paper, with the exception of a narrow horizontal slit—1 mm. wide approx.—about 1.5 cm. above the level of the bottom of the cylinder. Parallel to the end ( $\beta$ ) of the tank and distant about 10 cm. was clamped a similar slit illuminated by a filament lamp. Thus a shallow parallel beam of light could be directed on the under face of the water/air surface at any part desired, by raising or lowering the lamp and second slit. By this means the light was made to fall on the surface at the same vertical section of the cylinder for different levels of water.

The level of the water was read by means of a microscope focussed on the meniscus in the manometer tube F, which was backed by a mm. scale. The microscope eyepiece was graduated to 0.1 mm.

The glass tank, tubing, and reservoir were cleaned by alternately scrubbing half-a-dozen times with concentrated nitric acid and warm potassium bichromate solution, and then washing vigorously in tap water. The rubber tubing had steam passed through it for three hours, and was then left soaking in tap water.

To coat the cylinder with wax, the pulleys L and C, with their axle, were removed from the support DD'. The cylinder was then slightly immersed in a dish of molten wax and slowly spun until a coating about 3 or 4 mm. thick was deposited. It was then placed in a closed fume-chamber to cool. It was afterwards centred accurately in a lathe and turned smooth. Its diameter was measured by vernier callipers, three readings being taken at intervals of approximately  $60^\circ$ . The mean value was taken as  $d$ .

### *Method of Procedure.*

#### CASE I.—*Cylinder stationary.* Giving $\theta$ .

The cylinder A and pulleys C and L with axle were now replaced in the apparatus, and the tap M opened. Water from the tank was sucked into the siphon F F'. An electric lamp was placed behind the tank (fig. 1) at about the level

of the bottom of the cylinder, and the tank viewed from in front. The lowest generator of the cylinder and its image in the upper surface of the water were observed gradually approaching as the water-level rose. When they had approached to within about 2 mm., the rate of inflow of the water was cut down by the tap M. When the generator and its image just touched, the tap was closed. It was observed that immediately this happened, the water jumped up the wax surface to a height of 1-1.5 mm., owing to the fact that here the angle between the tangent plane to the cylinder and the general surface of the water was greater than the angle of contact. The reading on the manometer was taken. It appears as A in the tables of results.

The lamp was replaced behind the slits and the tap opened. The image of the slit on face ( $\beta$ ) in the lower face of the air/water and water/wax surfaces was then carefully observed through the end ( $\alpha$ ) of the tank.

At first, when the air/water surface was convex downwards, as in fig. 2(a), the meniscus portion behaved as a convex mirror to the incident light, and the line of contact of air/water/wax appeared as in fig. 2(b). On

Fig. 2.

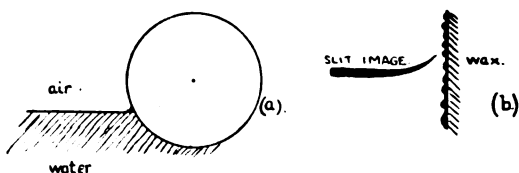
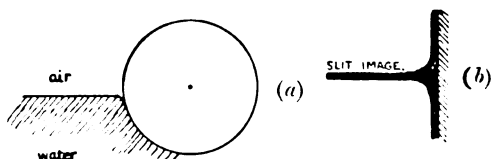


Fig. 3.



still raising the water-level slowly, the image gradually straightened out and extended right up to the line of contact, and the blurs with their light contours due to slight irregularities in the wax reduced to a minimum. The air/water surface was then regarded as a horizontal plane. The second slit and the lamp had been lowered so that the light was still incident on the same vertical

section of the cylinder as before. The height of the water in the manometer was read, giving readings B. The difference (B-A) gave the value  $h$ .

From this the value of  $\theta = \cos^{-1} \left( 2 \frac{h}{d} - 1 \right)$  was calculated.

This value,  $\theta$ , is the angle of contact as generally accepted.

CASE II.—*Cylinder rotated anti-clockwise.* Giving  $\theta_1$ .

With the water-level corresponding to the value  $\theta$  (Case I.), if the cylinder were rotated anti-clockwise the meniscus on the left of the cylinder became convex upwards, corresponding to an increase in the value of the contact angle; whilst that on the right became concave upwards, corresponding to a decrease in the angle.

The former case is analogous to a rising meniscus and the latter to a falling meniscus.

The left-hand side was always observed.

The water-level was lowered by placing the reservoir lower than the tank and opening the tap M. At first the appearance of the image of the slit and line of contact of air/water/wax was as in fig. 3 (b), the water/air surface near the wax acting as a concave mirror. As the water-level was lowered, the widening-out of the image diminished, and the light along the contour decreased to a minimum. At a critical level a perfect image was seen right up to the line of contact. The tap M was closed and the motion stopped. The level B was read on the manometer. (B-A), as before, gave  $AB = h$ , and the value of  $\cos^{-1} \left( 2 \frac{h}{d} - 1 \right) = \theta_1$  was calculated.

This gave  $\theta_1$ , the maximum value of the contact angle for the corresponding speed of rotation.

By stopping the motor immediately a value of B was obtained, it was possible to obtain several readings with the portion of the surface which had not been wetted.

CASE III.—*Cylinder rotated clockwise.* Giving  $\theta_2$ .

The motion was reversed by replacing the belt from pulleys to Z by a crossed belt. The same procedure as in Case II. was adopted, except that, as the meniscus was at first concave upwards, the reservoir had to be placed higher than the tank so that the water-level could be raised. The same number of readings was taken as in Case II.; but in order that they might be taken in pairs

according to the portion of the wax surface at the line of contact, the readings were set down in the table in the reverse order: the first reading here corresponds to the last reading in Case II., and so on.

In this case,  $\cos^{-1}\left(2\frac{h}{d}-1\right) = \theta_2 =$  minimum value of contact angle for this speed.

Values of  $\theta$  were determined before and after each complete set of  $\theta_1$  and  $\theta_2$ . The temperature of the water was also taken before and after the experiments, and the mean value taken.

TABLE I.

$$d = \begin{cases} 7.75 \\ 7.75 \\ 7.75 \end{cases} = 7.75 \text{ cm.} \quad \begin{array}{l} \text{Initial Temp.} = 10^{\circ} 3 \text{ C.} \\ \text{Mean Temp.} \\ \text{= } 10^{\circ} 5 \text{ C.} \end{array} \quad \left. \vphantom{\begin{array}{l} \text{Initial Temp.} \\ \text{Mean Temp.} \end{array}} \right\} = 10^{\circ} 4 \text{ C.}$$

1 revolution of Cylinder in 303 secs.

$$\therefore v = 0.8036 \text{ mm./sec.}$$

A.	B.	AB=h.	$\left(2\frac{h}{d}-1\right)$ .	$\cos^{-1}\left(2\frac{h}{d}-1\right)$ .	$\left(\frac{\theta_1+\theta_2}{2}\right)$ .	$(\theta_1+\theta_2)$ .
3.935	6.310	2.375	-.3871	112° 47'	104° 35'	16° 25'
„	7.380	3.445	-.1110	96° 22'		
„	6.285	2.350	-.3935	113° 10'	104° 42'	16° 57'
„	7.390	3.455	-.1084	96° 13'		
„	6.30	2.365	-.3897	112° 56'	104° 33'	16° 47'
„	7.395	3.460	-.1071	96° 9'		
„	6.310	2.375	-.3871	112° 47'	104° 30'	16° 34'
„	7.390	3.455	-.1084	96° 13'		
„	7.305	2.370	-.3884	112° 51'	104° 35'	16° 33'
„	7.385	3.450	-.1097	96° 18'		
„	6.290	2.355	-.3923	113° 6'	104° 44'	16° 44'
„	7.38	3.445	-.1110	96° 22'		
3.935	6.84	2.905	-.2503	104° 30'		
3.935	6.835	2.90	-.2516	104° 34'		

Mean .....  $\theta = 104^{\circ} 32'$

„ .....  $\theta_1 = 112^{\circ} 56'$

„ .....  $\theta_2 = 96^{\circ} 16'$

$$\therefore \frac{1}{2}(\theta_1 + \theta_2) = 104^{\circ} 36'$$

$$\therefore (\theta_1 - \theta_2) = 16^{\circ} 40'$$

The speeds of rotation were determined by timing one complete revolution of the cylinder by means of a stop-watch.

After a complete set of readings of  $\theta$ ,  $\theta_1$ , and  $\theta_2$  at a given speed, the cylinder was scraped and then recoated and turned, and the tank and tubing washed with tap water. When not in use, the tank and tubing were left in running water.

TABLE II.

Summary of Mean Values.

The figures in line I. are the mean values from Table I., and so on.

	$v$ .	$-\cos \theta_1$ .	$-\cos \theta_2$ .	$-\cos \theta$ .	$\theta_1$ .	$\theta_2$ .	$\theta$ .	$\frac{1}{2}(\theta_1 + \theta_2)$ .	$(\theta_1 - \theta_2)$ .
	mm./sec.				° '	° '	° '	° '	° '
I.	0.1273	.3321	.1663	.2513	109 24	99 34	104 33	104 29	9 50
II.	0.1943	.3506	.1522	.2517	110 31	98 45	104 34½	104 38	11 46
III.	0.3113	.3769	.1234	.2497	112 8½	97 5	104 28	104 37	15 3½
IV.	0.441	.3933	.1114	.2494	113 10	96 22	104 25	104 46	16 48
V.	0.641	.3904	.1097	.2516	112 59	96 18	104 34	104 38½	16 41
VI.	0.8036	.3897	.1093	.2510	112 56	96 16	104 32	104 36	16 40
VII.	1.06	.3935	.1087	.2513	113 10	96 15	104 34	104 42½	16 55
VIII.	1.472	.3920	.1110	.2523	113 5	96 23	104 37	104 44	16 42
IX.	1.969	.3940	.1104	.2516	113 13	96 20	104 34	104 46	16 53
X.	2.378	.3977	.1090	.2516	113 26	96 16	104 34½	104 51	17 10
XI.	2.43	.3936	.1148	.2501	113 11	96 36	104 29	104 53	16 35
XII.	3.586	.3918	.1127	.2532	113 4	96 29	104 49	144 46	16 35
XIII.	3.926	.3948	.1063	.2523	113 15	96 6	104 36½	104 40	17 9

In lines IV. to XIII. it is obvious that  $\theta_1$ ,  $\theta_2$ ,  $\frac{1}{2}(\theta_1 + \theta_2)$ , and  $(\theta_1 - \theta_2)$  are constant.

Thus for speeds  $> .44$  mm./sec. (taking the average values):

$$\begin{aligned}\theta_1 &= 113^\circ 9', \\ \theta_2 &= 96^\circ 20', \\ (\theta_1 - \theta_2) &= 16^\circ 49' .\end{aligned}$$

The wax used was a specimen of Kohlbaum's Purified Paraffin-Wax of melting-point  $56^\circ.7$  C., being the mean of six determinations lying between  $56^\circ.6$  C. and  $56^\circ.85$  C. The author is indebted to Professor I. M. Heilbron for the specimen.



*Discussion of the Results.*

The following are the results obtained for water at  $10^{\circ}$  C. :—

Angle of contact  $\theta$  when the cylinder

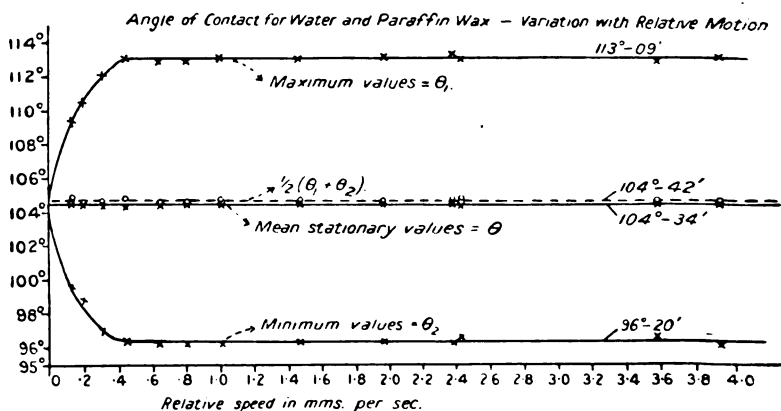
is stationary . . . . . =  $104^{\circ} 34'$ ,

being the mean of thirty observations lying between  $104^{\circ} 21'$  and  $104^{\circ} 52'$ , twenty of the readings lying between  $104^{\circ} 30'$  and  $104^{\circ} 40'$ .

A specimen set of observations taken whilst the cylinder was in motion is given in Table I.

In all, observations were made at thirteen different speeds, the results being summarized in Table II. and Graph I. The values of  $\theta_1$ ,  $\theta_2$ ,  $\frac{1}{2}(\theta_1 + \theta_2)$ ,  $(\theta_1 - \theta_2)$  there given are the mean values at the stated speed, whilst  $\theta$  is the mean of readings taken before and after the experiment.

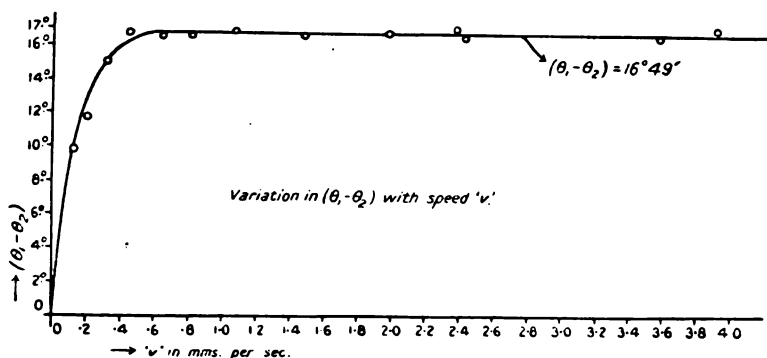
Graph I.



Graph I. shows very clearly that at all speeds the maximum value of the contact angle  $\theta_1$  and the minimum value  $\theta_2$  are equidistant from the stationary value  $\theta$ ; and that  $\frac{1}{2}(\theta_1 + \theta_2)$  agrees, within the range of experimental error, with the value  $\theta$ . It is also clear that for speeds  $> 0.44$  mm./sec., both  $\theta_1$  and  $\theta_2$  are constant, being equal to  $113^{\circ} 9'$  and  $96^{\circ} 20'$  respectively. It is therefore concluded that there exists both a maximum and a minimum angle of contact, in addition to the angle of contact  $\theta$  usually found, their values in the case of paraffin-wax and water being as stated above.

Graph II. shows the change in  $(\theta_1 - \theta_2)$  with  $v$ , again pointing to the same conclusion.

Graph II.



### Possible Error.

The possible error amounted to a difference of .005 cm. in the value of  $h=AB$ , which leads to a possible error of  $\pm 5$  minutes in the angles.

Thus it may be taken that

$$\theta = 104^\circ 34' \pm 5',$$

$$\theta_1 = 113^\circ 9' \pm 5',$$

$$\theta_2 = 96^\circ 20' \pm 5'.$$

The average deviations from the mean values are: for  $\theta=3'$ ,  $\theta_1=6'$ , and  $\theta_2=6'$ .

The only other results for paraffin-wax and water within the knowledge of the writer are:  $\theta=105^\circ$  (Coghill and Anderson, "Molecular Physics of Ore Flotation," J. Phys. Chem. xxii. p. 249, April 1918), and  $\theta=106^\circ 57'$  as the means of four values ranging from  $106^\circ 8'$  to  $107^\circ 41'$  by the depression of water in a waxed tube and  $\theta=106^\circ 28'$  by the tilting-plate method (Hartley and Bosanquet, Phil. Mag. No. 249, Sept. 1921, p. 458).

### Conclusion.

Various writers have noted a difference between the heights of the liquid in a capillary tube according as there is a rising or a falling meniscus; others, a difference between the thicknesses of drops of the same size according as the drops are expanding or contracting. The results here given provide an explanation of these differences.

Harkins and Brown, in "The Determination of the Surface Tensions of Water and Benzene by Capillary Height Methods" (Journ. Amer. Chem. Soc. xii. p. 499), state: "The rise for a falling meniscus was always greater than for a rising meniscus in the same sample of water, so only the former was used."

In the case of these liquids,  $\theta_2=0$  but  $\theta_1$  does not, as there will be a finite maximum angle, though it may be small. In the falling meniscus, where the walls have been in previous contact with the liquid,  $\theta_2=0$ ; but in the rising meniscus the contact angle is not  $\theta_2$ , but  $\theta_1$  and finite.

Thus  $\cos \theta_1$  is  $< \cos \theta_2$ , and therefore  $T \cos \theta_1 < T \cos \theta_2$ ; and therefore the height in the falling meniscus case will be greater than for the rising meniscus in the ratio  $\cos \theta_2 : \cos \theta_1$ .

Allan Ferguson, in "Studies in Capillarity—II." (Faraday Soc. Trans. Feb. 1921), dealing with a method of adjusting the air-pressure to force the meniscus down to the level of the free liquid surface, says:—"The presence or absence of a constant error was tested by taking the mean of the readings, (1) when the meniscus just disappeared within the tube, (2) when it just protruded from the tube. The mean of these pressures agreed satisfactorily with the 'crucial' pressure."

The results given in the present paper explain this. Taking for granted that  $\theta_2=0$  for water,  $\theta_1$  finite but small, then, as before,  $T \cos \theta$  should agree with  $\left( \frac{T \cos \theta_1 + T \cos \theta_2}{2} \right)$ .

Many writers insist on the necessity for tapping the capillary, or the plate on which a drop rests, before taking readings, but give no reason beyond that it pays to do so—*e. g.*, Hartley and Bosanquet, in the paper already cited, when determining  $\theta$  for water and azobenzene by the measurement of a drop, state: "The necessity for tapping the plate is shown by the following two readings taken without tapping:—

Expanding drop	. . . 0.396 cm.,	} (Thickness of the drop.)
Contracting drop	. . . 0.270 cm."	

Here again, in the expanding drop, the water is creeping over fresh solid surface, and the angle of contact is the maximum  $\theta_1$ , whilst in the contracting drop the angle to be taken is the minimum  $\theta_2$ . The result obtained by tapping would correspond to  $\theta$  and would be the same as the

mean of the results  $\theta_1$  and  $\theta_2$ , since it has been shown that  $\theta = \frac{1}{2}(\theta_1 + \theta_2)$ . In fact, the mean of the two readings given—0.333 cm.—agrees with the mean value obtained by tapping as used by the writers named, viz. 0.335 cm.

### *Note on Wetting.*

Notwithstanding that "wetting" has become such an important factor in connexion with the Flotation of Minerals and also in lubrication, the term is often used in a very loose manner. The writer has not been able to obtain a definite statement as to the meaning of "wetting." Many writers tacitly assume that a liquid that "wets" a solid makes with it a zero contact angle. Cp. Edser, 'General Physics,' p. 312, and Richards & Carver (Journ. Amer. Chem. Soc. xliii. 1921, p. 827 *et seq.*). Others assume that a liquid "wets" a solid when  $\theta < 90^\circ$ , and does not "wet" it when  $\theta > 90^\circ$ .

Clerk Maxwell, in the article on Capillarity in the Encycl. Britannica, states the question thus:—"If a small quantity of a fluid stand in a drop on the surface of a solid without wetting it, the angle of contact is  $180^\circ$ ; if it spreads over the surface and wet the solid, the angle of contact is zero."

With regard to this statement, there is no known combination of liquid and solid where  $\theta = 180^\circ$  (unless the solid surface be dusty): thus, in Maxwell's sense, there is no case where the fluid rests on the solid without wetting it. On the other hand, most combinations of liquid and solid give a value of  $\theta$  intermediate between  $0^\circ$  and  $180^\circ$ . The cases might therefore be distinguished as "non-wetting" ( $\theta = 180^\circ$ ), "partial wetting" ( $\theta$  finite), and "complete wetting" ( $\theta = 0$ ). Still this does not give any real physical significance to the term "wetting."

From the fact that  $\theta_1$  is  $> \theta_2$ , it follows that the surface energy of the air/solid interface has been increased by having been in contact with the liquid. From this it is concluded that the solid has absorbed or imbibed some of the liquid. It then follows that if the solid be moved relative to the liquid in a direction tangential to the interface, for example by a clockwise rotation of the waxed cylinder in the experiments previously described, that portion leaving the liquid will tend to drag the liquid with it up to the limit of the force of cohesion of the liquid or of the adhesion between liquid and solid, whichever is the greater. Thus the contact angle on the leaving

side will be decreased towards  $\theta_2$  and that on the entering side increased towards  $\theta_1$ . When separation does take place, the contact angle in the former case will be the minimum value  $\theta_2$ , and in the latter case the maximum value  $\theta_1$ , for that particular speed.

Thus the results obtained strongly support the view that this variation in the contact angle is due to absorption or imbibition of the liquid by the solid. Such a phenomenon is true "wetting," and, as is evident from these experiments, is possible for obtuse as well as acute angles of contact—degree of wetting depending on the range ( $\theta_2 - \theta_1$ ), that is to say on the degree to which the surface energy of the solid is affected on coming into contact with the liquid.

These experiments are to be repeated with other combinations of solids and liquids.

The author desires to thank Professor L. R. Wilberforce, M.A., for his kindly criticism and advice during this investigation.

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XXVI. *The Second Virial Coefficient of Gases.* By ANGUS F. CORE, *Chemical Department, The University, Manchester* \*.

THE equation of state of a perfect gas is  $pv = RT$ , where  $p$  is the pressure,  $v$  the volume occupied by the unit of quantity,  $T$  the absolute temperature, and  $R$  the gas constant for the unit of quantity. This is a limiting relation which we may suppose that the behaviour of all real non-dissociating gases approaches as the volume becomes very great.

The equation of state of any gas may be written in the form

$$pv = A + \frac{B}{v} + \frac{C}{v^2} + \dots,$$

where  $A$ ,  $B$ ,  $C$ , etc. are called the first, second, third, etc. virial coefficients. These coefficients are functions of  $T$  but not of  $v$ . The value of  $A$  for a non-dissociating gas, with which only are we concerned, is necessarily  $RT$ ; the same for the gram molecule of all gases.

\* Communicated by Prof. S. Chapman.

It is the object of the present discussion to deduce the value of the second virial coefficient, in the first place of a gas with molecules of a spherically symmetrical type, and then of a gas with molecules of a general type. In the very special case of a gas consisting of hard spherical molecules exerting no attraction on each other, the third coefficient,  $C$ , is readily found. The results agree with those obtained by Keesom\* and others, but the method is comparatively simple.

The kinetic significance of what is known in thermodynamics as "activity" is shown in the paper.

In the last section an expression has been obtained for the second virial coefficient of a binary mixture of gases.

### *Preliminary.*

Suppose that in a vessel of unit volume, kept at a uniform temperature  $T$ , there are  $\nu$  molecules of a gas. Then if the molecules are non-attracting mass points, and if no external forces act on them, except those exerted by the walls of the containing vessel, the molecular concentration is everywhere  $\nu$ . By this statement it is not meant that in any volume element,  $dv$ , there are  $\nu dv$  molecules, since, evidently, the chances are against there being any of the molecules in the particular element at a given instant. What is meant is that the probability of there being one molecule in the element  $dv$  at any instant is  $\nu dv$ . That is to say, if we could take a very large number,  $A$ , of instantaneous views of the element  $dv$  we should observe a point molecule in it  $A\nu dv$  times; or if there were  $A$  exactly similar unit vessels each containing  $\nu$  molecules, then at any instant there would be  $A\nu dv$  of them with a molecule in a particular element  $dv$ .

Suppose, now, that external forces act on the molecules, of a kind that can be derived from a permanent field of potential. Then the molecules will no longer be distributed uniformly over the unit volume. If the work required to bring a single molecule from a region taken to be of zero potential to a given point is  $\chi$ , then  $\chi$  is the potential at that point, and according to the classical theory of statistical mechanics the molecular concentration there is equal to

$$\nu_0 e^{-\chi/kT},$$

where  $T$  is the temperature and  $k$  the gas constant per molecule. Putting  $\chi=0$  it will be seen that  $\nu_0$  is the molecular

\* W. H. Keesom, Proc. Sect. of Sciences, Amsterdam, vol. xv. (1) pp. 240, 256.

concentration in regions of zero potential. In this expression  $\chi$  is the potential due to an external field which does not vary with the time. This result can be extended in the following way.

Let the molecules be such that they exert forces on each other depending only on the distances separating their centres. Then round each centre there is a field of potential with respect to another molecule. The instantaneous potential,  $\chi$ , at any point, due to another molecule or other molecules, is defined to be the work required to bring the centre of a single molecule from a region of zero potential up to that point while the other molecule or molecules are kept fixed in position. Consider, then, the  $\nu$  molecules at any instant. They are in definite positions and consequently there is a definite instantaneous potential with respect to another single molecule. Let another molecule be added to the vessel, so that there are now  $\nu + 1$  molecules. Then if we regard only those moments in the history of the first  $\nu$  molecules in which they have these same positions, it is shown by statistical mechanics that the probability that the centre of the single molecule is in an element of volume  $dr$ , where the instantaneous potential is  $\chi$ , is proportional to

$$e^{-\chi/kT} dr,$$

just as when the field is a permanent external one.

The theorem may be further extended so as to include molecules which exert forces on each other depending not only on the distance separating them but also on their orientations in any way. Just as before, we choose instants when the  $\nu$  molecules are always in the same positions, not now as regards only the points taken as their centres, but also as regards their exact orientations. We cannot now speak of the potential of the remaining molecule at any point, for this does not depend only on the position of the molecule's centre, but also on its orientation. Nevertheless, it is shown that if we further restrict the instants of viewing the system to instants when the single molecule is orientated in a particular way, then the probability of its centre being in the element of volume  $dr$  is proportional to

$$e^{-\chi/kT} dr,$$

$\chi$  being the now perfectly definite quantity of work required to bring the centre of the single molecule orientated in this definite way into the element of volume  $dr$ .

*Spherically Symmetrical Molecules.*

Imagine a single molecule in a vessel of unit volume, this volume being very large compared with the molecular field. Then if the potential throughout the vessel is uniform, the probability that at any instant the centre of the molecule lies in an element of volume  $dv$  is equal to  $dv$ . The molecular concentration is everywhere equal to 1.

Now suppose that there are  $\nu$  other identical molecules in the vessel. Then if we regard the first molecule only at those instants when the other  $\nu$  molecules are always in the same positions, its concentration is no longer uniform but is equal to

$$P_0 e^{-\chi/kT},$$

where  $\chi$  is the instantaneous potential due to the other molecules, and  $P_0$  is the concentration in regions of zero potential, which will be taken to be those regions outside the field of any molecule. It is evident that, since this concentration refers to one molecule in a vessel of unit volume, if it be integrated with respect to the volume over the whole unit volume the result must be 1. Therefore for finding  $P_0$  we have the equation

$$P_0 \int e^{-\chi/kT} dv = 1,$$

the integration being taken over the whole interior of the vessel. Now, outside the field of a molecule the potential  $\chi$  is zero, and therefore

$$(1 - e^{-\chi/kT}) = 0.$$

Therefore the above equation is conveniently put into the form

$$P_0 \int \{1 - (1 - e^{-\chi/kT})\} dv = 1.$$

This is equivalent to

$$P_0 \{1 - \int (1 - e^{-\chi/kT}) dv\} = 1,$$

since the integration is through a unit of volume. Thus

$$P_0 = \frac{1}{1 - \int (1 - e^{-\chi/kT}) dv}.$$

This, therefore, gives the concentration of the single molecule at all points outside the influence of any other molecule for a particular arrangement of these other molecules. Now in any real case  $\nu$  is very large and the statistical arrangement of the molecules practically never varies appreciably from



a certain most probable arrangement. Consequently we may assume that

$$\int (1 - e^{-x/kT}) dv$$

does not vary with the time. Therefore we may write

$$\int (1 - e^{-x/kT}) dv = f(\nu, T),$$

$f(\nu, T)$  being a function of  $\nu$  and  $T$  only, for a given kind of molecule. Thus the presence of the other  $\nu$  molecules raises the concentration of the first molecule in regions of zero potential from 1 to

$$\frac{1}{1 - f(\nu, T)}.$$

Now, since all the molecules are exactly alike, it is evident that this applies to each one of them. Therefore the total concentration of the molecules in regions of zero potential must be given by

$$\nu_c = \frac{\nu + 1}{1 - f(\nu, T)} \quad \text{or} \quad \frac{\nu}{1 - f(\nu, T)},$$

since  $\nu + 1$  is indistinguishable from  $\nu$ .

The evaluation of  $f(\nu, T)$  in any particular case is the chief difficulty of the problem.  $\nu_0$  and  $\nu$  are converted into the corresponding gram molecular quantities,  $A$  and  $C$ , by the substitutions  $A = \nu_0/N$ ,  $C = \nu/N$ , in which  $N$  is the number of molecules in the gram molecule. Thus

$$A = \frac{C}{1 - f(\nu, T)}.$$

Before considering the value of  $f(\nu, T)$  we shall obtain a relation by means of which the pressure may be calculated when the concentration,  $C$ , and  $A$  are known.

The required relation is obtained directly as follows:—Imagine a column of the gas standing in the gravitational field of the Earth. Let “ $z$ ” be the height measured above any given level. Then if “ $m$ ” is the mass of a single molecule, we have the hydrodynamical relation

$$dp = CNmg dz. \quad . \quad . \quad . \quad . \quad . \quad (a)$$

Now in general there are two sorts of field acting simultaneously on the molecules: the gravitational field and the inter-molecular fields.  $A$  is the concentration outside the inter-molecular fields and therefore in regions where the potential is that due to the gravitational field alone. This

potential is equal to  $mgz$ . Therefore the value of  $A$  at any height  $z$  is given by

$$A = A_0 e^{-mgz/kT}.$$

Therefore

$$kT d \log A = mg dz, \text{ or } RT d \log A = Nmg dz, \quad (b)$$

where  $R$  is the gas constant per gram molecule. Combining (a) and (b) we obtain the required relation

$$\frac{dp}{C} = RT d \log A.$$

It may be noticed that this result enables us to identify  $A$  with the quantity known in thermodynamics as the "activity" of the gas.

Since

$$A = \frac{C}{1-f(v, T)}.$$

Therefore

$$\frac{dp}{C} = RT d \log \frac{C}{1-f(v, T)}.$$

If then we can find the value of  $f(v, T)$  the integration of this equation will yield the value of the pressure.

Now

$$f(v, T) = \int (1 - e^{-\chi/kT}) dv,$$

the integration being taken over the whole interior of a vessel of unit volume containing  $v$  molecules, and  $\chi$  being the instantaneous potential due to these molecules.  $f(v, T)$  is a very difficult quantity to calculate for the following reason. Although  $(1 - e^{-\chi/kT})$  is very small except quite close to a molecule, nevertheless at any instant some molecules will be close enough to one or more other molecules to cause parts of their fields where the potentials are not small to overlap. This makes the evaluation of the integral in the above equation exceedingly difficult.

But when the gas is not too concentrated it is allowable to neglect the overlapping of molecular fields in this estimation; or at any rate of the overlapping of those parts where the potentials are not small. The error so introduced will not affect the second virial coefficient, being of the same order of magnitude as the third coefficient. To this degree of approximation, therefore, we may write

$$f(v, T) = v \int (1 - e^{-\chi/kT}) dv = v\phi(T),$$

the integration being taken not over the whole interior

of the vessel but over the field of a single molecule.  $\phi(T)$  is, for a particular kind of molecule, a function of the temperature only.

Write  $\Phi(T) = N\phi(T)$ . Then

$$A = \frac{C}{1 - C\Phi(T)}.$$

Therefore, for finding the pressure, we have the relation

$$\frac{dp}{C} = RT d \log \frac{C}{1 - C\Phi(T)}.$$

The solution of this gives

$$p = - \frac{RT}{\Phi(T)} \log (1 - C\Phi(T)). \quad (c)$$

If the interference of molecular fields had not been neglected, instead of  $\Phi(T)$  we should have obtained a series of ascending powers of  $C$ :

$$\Phi_1(T) + \Phi_2(T)C + \Phi_3(T)C^2 + \dots$$

Therefore to the required degree of accuracy the relation (c) is equivalent to

$$p = RTC + \frac{1}{2}RTC^2\Phi(T). \quad (d)$$

The expression for the pressure given in (c) is interesting inasmuch as in obtaining it the only error made has been the neglect of the simultaneous approach of three or more molecules. The error of assuming uniform concentration up to the wall of the containing vessel has not been made. The two errors are, however, of the same order of magnitude.

If we compare (d) written in the form

$$pv = RT + \frac{RT\Phi(T)}{2v} \quad \text{with} \quad pv = RT + B/v,$$

it will be seen that the second virial coefficient is given by

$$B = \frac{1}{2}RT\Phi(T).$$

The function  $\Phi(T)$ , that is

$$N \int (1 - e^{-\chi \cdot kT}) dr,$$

must be evaluated for any particular type of molecule by writing for  $\chi$  the corresponding function of the distance " $r$ " separating the centres of two molecules. In place of the differential  $dv$  we substitute  $4\pi r^2 dr$ , and integrate from  $r=0$

to  $r=\infty$ ; that is, to a value of  $r$  sufficiently great to make  $(1-e^{-\chi/kT})$  negligible.

We shall first consider a type of molecule that will give an equation of state, so far as the second virial coefficient, of the same form as the equations of van der Waals and Dieterici. Both these equations as far as the second order terms may be written

$$pv = RT + \frac{RT}{v} - \frac{a}{v}.$$

It will be seen on comparing this with the general expression that the term  $B/v$  in the latter is represented in this equation by two terms: one proportional to  $T$ , the other independent of  $T$ . In general this will not be the case. But suppose that from  $r=0$  to  $r=\sigma$ ,  $\chi/kT$  is very great, and that for  $r>\sigma$ ,  $\chi/kT$  is everywhere small. The integral

$$N \int (1-e^{-\chi/kT}) dv = 4\pi N \int_0^\infty (1-e^{-\chi/kT}) r^2 dr$$

then divides into two parts:—

$$4\pi N \int_0^\sigma (1-e^{-\chi/kT}) r^2 dr, \quad \text{where } \chi/kT \text{ is very great,}$$

and

$$4\pi N \int_\sigma^\infty (1-e^{-\chi/kT}) r^2 dr, \quad \text{where } \chi/kT \text{ is small.}$$

Therefore approximately

$$\Phi(T) = \frac{1}{3}\pi N\sigma^3 + \frac{4\pi N}{kT} \int_\sigma^\infty \chi r^2 dr$$

and

$$pv = RT + \frac{2RT\pi N\sigma^3}{3v} + \frac{2\pi N^2 \int_\sigma^\infty \chi r^2 dr}{v}.$$

Under these circumstances, then,  $B$  separates into two parts, one of which is nearly proportional to  $T$  and the other nearly independent of  $T$ , just as in the equation of van der Waals. This is because part of the field consists of a region of very high potential and the rest is a region of small potential. It is evident that the higher the temperature the more completely does the second part become independent of  $T$  and also that the first part becomes less closely proportional to  $T$ . Comparing the two equations it will be seen that the “ $b$ ” of van der Waals equals  $\frac{2}{3}\pi N\sigma^3$ , that is 4 times the

actual "volume" of the molecules in the gram molecule ; and that the "a" of van der Waals equals

$$-2\pi N^2 \int_{\sigma}^{\infty} \chi r^2 dr.$$

In general B does not divide in this way. Thus consider the case of a gas which consists of molecules which attract or repel each other according to an inverse power of the distance separating their centres. Suppose that the molecules are perfectly hard and of diameter  $\sigma$ , and that for values of  $r$  greater than  $\sigma$  two molecules attract each other with a force proportional to  $1/r^{q+1}$ . Let  $\chi_{\sigma}$  be the work required to separate two molecules in contact to an infinite distance apart. Then

$$\chi = \infty \quad \text{for } r < \sigma,$$

$$\chi = -\chi_{\sigma} \left( \frac{\sigma}{r} \right)^q \quad \text{for } r > \sigma.$$

In this case therefore

$$\Phi(T) = 4\pi N \int_0^{\sigma} (1 - e^{-\chi/kT}) r^2 dr + 4\pi N \int_{\sigma}^{\infty} (1 - e^{-\chi/kT}) r^2 dr,$$

in which  $\chi$  stands for  $-\chi_{\sigma} \left( \frac{\sigma}{r} \right)^q$ .

This may be integrated by expanding  $e^{-\chi/kT}$  into a series of powers of  $\chi/kT$  and integrating term by term. Thus

$$\Phi(T) = 4\pi N \sigma^3 \left\{ 1 - \frac{3}{(q-3)} \frac{\chi_{\sigma}}{kT} - \frac{1}{2!} \frac{3}{(2q-3)} \left( \frac{\chi_{\sigma}}{kT} \right)^2 - \frac{1}{3!} \frac{3}{(3q-3)} \left( \frac{\chi_{\sigma}}{kT} \right)^3 - \dots \right\},$$

and therefore

$$pv = RT + \frac{RTb}{v} - \frac{3RTb}{v} \left\{ \frac{1}{(q-3)} \frac{\chi_{\sigma}}{kT} + \frac{1}{2!} \frac{1}{(2q-3)} \left( \frac{\chi_{\sigma}}{kT} \right)^2 + \frac{1}{3!} \frac{1}{(3q-3)} \left( \frac{\chi_{\sigma}}{kT} \right)^3 + \dots \right\}.$$

The solution fails when  $q < 3$ .

It will be observed that at temperatures sufficiently great to make  $\chi_{\sigma}/kT$  moderately small the relation approximates to

$$pv = RT + \frac{RTb}{v} - \frac{3N\chi_{\sigma}}{(q-3)v}.$$

*The Third Virial Coefficient for Spherically Symmetrical Molecules.*

In order to calculate the third term on the right-hand side of the equation

$$pv = RT + \frac{B}{v} + \frac{C}{v^2} + \dots$$

it is necessary to integrate

$$(1 - e^{-\chi/kT}) dv$$

over all the molecular fields, taking into account the proximity of two molecules. If this were done we should obtain for  $f(v, T)$  an expression of the form  $v\phi_1(T) + v^2\phi_2(T)$ , and therefore instead of  $\Phi(T)$  the expression

$$\Phi_1(T) + C\Phi_2(T) \quad \text{or} \quad \Phi_1(T) + \frac{1}{v}\Phi_2(T),$$

if  $1/v$  be substituted for  $C$ . The activity  $A$  is therefore given by

$$A = \frac{1}{\left(r - \Phi_1(T) - \frac{1}{v}\Phi_2(T)\right)},$$

and the corresponding differential relation between the pressure and volume is

$$vdp = RT d \log \left( \frac{1}{r - \Phi_1(T) - \frac{1}{v}\Phi_2(T)} \right).$$

The solution of this to the required approximation is

$$pv = RT + \frac{RT\Phi_1(T)}{2v} + \frac{RT}{3} \left( \frac{\Phi_1^2(T) + 2\Phi_2(T)}{v^2} \right). \quad (e)$$

To evaluate the coefficient  $\Phi_2(T)$  we may proceed in the following way. Fix the attention on one particular molecule of the  $v+1$  molecules contained in the vessel of unit volume. The probability that a second particular molecule at any instant has its centre within a distance between  $r$  and  $r+dr$  of the centre of the first molecule is with sufficient accuracy  $4\pi r^2 e^{-\chi/kT} dr$ . Therefore the probability that any one of the  $v$  molecules is so situated with respect to the first is  $4\pi v r^2 e^{-\chi/kT} dr$ . Therefore the number of molecules out of the whole number in unit volume which have such a neighbour is  $4\pi v^2 r^2 e^{-\chi/kT} dr$ . Therefore the number of pairs of

molecules whose centres are separated by a distance between  $r$  and  $r + dr$  is  $2\pi\nu^2 r^2 e^{-\chi/kT} dr$ .

When we integrate over the field of two molecules which are far apart, then

$$\int (1 - e^{-\chi/kT}) dv = 2\phi(T).$$

When  $r$  is not great this will no longer be the case, and the value of the integral taken over the combined field may conveniently be written  $2\phi(T) + g(r, T)$ , in which  $g(r, T)$  is a function of  $r$  and  $T$  depending on the molecular field. Thus every pair of molecules for which  $r$  is between  $r$  and  $r + dr$  contributes to the total integral  $f(\nu, T)$  the quantity  $g(r, T)$  in excess of their contribution when the component molecules are far apart.

Therefore, since the number of such pairs is  $2\pi\nu^2 r^2 e^{-\chi/kT} dr$ , the value of  $f(\nu, T)$  is given by

$$f(\nu, T) = \nu\phi(T) + 2\pi\nu^2 \int_0^\infty r^2 g(r, T) e^{-\chi/kT} dr.$$

Therefore

$$\Phi_1(T) = N \int (1 - e^{-\chi/kT}) dv,$$

the integration being taken over the whole field of a single molecule; and

$$\Phi_2(T) = 2\pi N^2 \int_0^\infty r^2 g(r, T) e^{-\chi/kT} dr.$$

When these two quantities have been evaluated they must be substituted in the equation (e).

If the molecules are simply hard elastic spheres of diameter  $\sigma$ , with no external field,  $\Phi_2(T)$  is readily found. In this case

$$\chi = \infty \quad \text{for } r < \sigma,$$

$$\chi = 0 \quad \text{for } r > \sigma,$$

$$g(r, T) = 0 \quad \text{for } r > 2\sigma.$$

Therefore

$$\Phi_2(T) = 2\pi N^2 \int_\sigma^{2\sigma} r^2 g(r, T) dr.$$

It may be easily shown that for values of  $r$  between  $\sigma$  and  $2\sigma$

$$g(r, T) = -\frac{\pi}{3} \left( 4\sigma^3 - 3\sigma^2 r + \frac{r^3}{4} \right).$$

Therefore

$$\Phi_2(T) = -\frac{17}{36}\pi^2 N^2 \sigma^6.$$

Also

$$\Phi_1(T) = \frac{1}{3}\pi N \sigma^3.$$

Writing as usual  $\frac{2}{3}\pi N \sigma^3 = b$ , this gives

$$\Phi_1(T) = 2b, \quad \Phi_2(T) = -\frac{1}{6}bh.$$

Substituting these values in equation (e) we obtain

$$pv = RT + RT \frac{b}{v} + \frac{5}{8} RT \left( \frac{b}{v} \right)^2.$$

### Molecules of a General Type.

By an extension of this method the virial of a gas consisting of molecules of a very general type may be found.

In each of the identical molecules we choose a point C as centre, and an axis, "*l*," passing through C; also a plane "*s*" containing the axis. These elements are similarly situated in all the molecules. Also let O be a fixed point in space, L a fixed direction, and S a plane containing L. Then the situation of the centre of a molecule is given by "*r*," the length OC;  $\theta_1$ , the angle between OC and L, that is the co-latitude of C; and  $\phi$  the longitude of C measured from the plane S. The element of volume is then

$$dv = r^2 \sin \theta_1 d\theta_1 d\phi dr.$$

The orientation of a molecule is given by  $\theta_2$ , the angle between the axis *l* and the direction L;  $\psi_1$  the angle between the plane S and the plane L, *l*;  $\psi_2$  the angle between the plane *s* and the plane L, *l*.

As before, suppose that there are  $\nu + 1$  molecules in a vessel of unit volume. Then instants are chosen, without regard to the position of the centre of a certain one of these molecules, but in which the arrangement of the other  $\nu$  molecules, both as regards the position of their centres and their orientations, is always the same, and in which, at the same time, the orientation of the single molecule is always within certain infinitesimal limits. We may now, as before, write down the probability that the centre of the particular molecule is in a given element of volume, *dv*, in one of these instants. For, as already stated, this probability is equal to

$$Be^{-\chi/kT} dv. \quad . \quad . \quad . \quad . \quad . \quad (f)$$



In this expression  $\chi$  is the work required to bring the centre of the molecule, orientated in the particular way, from a region outside the influence of any other molecule into the particular volume element  $dv$ .  $\chi$  is some definite function of the quantities  $\phi, \theta_1, \theta_2, \psi_1, \psi_2, r$ .  $B$  is a quantity, independent of the position of  $C$ , which is determined as follows.

When the single molecule is outside the influence of any other molecule the probability that  $\theta_2$  lies between the values  $\theta_2$  and  $\theta_2 + d\theta_2$  is  $\frac{1}{2} \sin \theta_2 d\theta_2$ . The probability that  $\psi_1$  is between  $\psi_1$  and  $\psi_1 + d\psi_1$  is  $\frac{1}{2\pi} d\psi_1$ ; and the probability that  $\psi_2$  is between  $\psi_2$  and  $\psi_2 + d\psi_2$  is  $\frac{1}{2\pi} d\psi_2$ . Therefore the probability that the molecule is simultaneously orientated between these limits is

$$\frac{1}{8\pi^2} \sin \theta_2 d\psi_1 d\psi_2 d\theta_2.$$

This may be written  $d\omega$  for short. If  $P_0$  is the "concentration" of this molecule in free space, then the probability that it is orientated in the above way, and that, simultaneously, its centre is in a particular element  $dr$  of free space, is therefore  $P_0 d\omega dv$ . Comparing this with (f), in which  $\chi$  is made equal to 0, we see that  $B = P_0 d\omega$ . Therefore the probability that the molecule is orientated and situated within the given limits is

$$P_0 e^{-\chi kT} d\omega dv.$$

The value of  $P_0$  is found, exactly as in the case of spherically symmetrical molecules, as follows.

Since the above probability refers to a single molecule, therefore

$$P_0 \int e^{-\chi kT} d\omega dv = 1,$$

the integration being taken over all orientations and the whole volume of the vessel. Since the vessel is of unit volume and large compared with the field of a molecule,

$$P_0 = \frac{1}{1 - f(v, T)},$$

in which

$$f(v, T) = \int (1 - e^{-\chi kT}) d\omega dv.$$

The activity,  $A$ , is given by

$$A = \frac{C}{1 - f(\nu, T)}.$$

Also as before,

$$dp/C = RT d \log A.$$

When the gas is not too concentrated, so that we may neglect triple encounters, then

$$f(\nu, T) = \nu \phi(T),$$

$\phi(T)$  being the value of the above integral taken, not throughout the whole volume of the vessel, but over the whole field of a single molecule.

The integral involves the relative positions of two molecules. We may consider one molecule to be fixed with its centre  $C_1$  in the point of origin  $O$ , and with its axis  $l_1$  and reference plane  $s_1$  to coincide with the fixed direction  $L$  and plane  $S$ . Then  $r$  is the distance  $C_1C_2$  between the centres of the two molecules;  $\theta_1$  is the angle between  $C_1C_2$  and the axis  $l_1$ ;  $\phi$  is the angle which the plane containing  $l_1$  and  $C_1C_2$  makes with the plane  $s_1$ . Also  $\theta_2$  is the angle between the two axes  $l_1$  and  $l_2$ ;  $\psi_1$  and  $\psi_2$  the angles between the plane of the two axes and the planes  $s_1$  and  $s_2$  respectively.

Then

$$\phi(T) = \frac{1}{8\pi^2} \int_0^{2\pi} \int_0^{2\pi} \int_0^\pi \int_0^\pi \int_0^{2\pi} \int_0^\infty (1 - e^{-\chi kT})^2 \sin \theta_1 \sin \theta_2 d\psi_1 d\psi_2 d\theta_1 d\theta_2 d\phi dr.$$

Without altering the form of the above expression it is possible to alter the meaning of some of the symbols so that the two molecules are involved symmetrically. As before,  $r$  is the distance  $C_1C_2$  between the two centres.  $\theta_1$  and  $\theta_2$  are the angles which the axes  $l_1$  and  $l_2$  make with the line of centres;  $\phi$  the angle between the two planes  $l_1, C_1C_2$  and  $l_2, C_1C_2$ , that is between the two planes which contain the line of centres and the two axes; and  $\psi_1$  and  $\psi_2$  the angles which the planes  $s_1$  and  $s_2$  make with the planes  $l_1, C_1C_2$  and  $l_2, C_1C_2$  respectively.

If now we write  $N\phi(T) = \Phi(T)$  we obtain, exactly as in the case of molecules of spherical symmetry,

$$pv = RT + \frac{RT\Phi(T)}{2v}.$$

The working out of any actual case will usually be complicated. It will be sufficient here to give the result \* when the gas consists of hard spherical molecules at the centre of each of which is an electric doublet of constant moment. In this case the potential function  $\chi$  will not contain the angles  $\psi_1$  and  $\psi_2$ . If  $\sigma$  is the diameter of the molecules, and if  $\chi_\sigma$  is the work required to separate to infinity two molecules placed in contact with the axes of the doublets parallel and at right angles to the line of centres, then writing  $\frac{2}{3}\pi N\sigma^3 = b$ ,

$$pv = RT + \frac{RTb}{v} - \frac{RTb}{v} \left\{ \frac{1}{3} \left( \frac{\chi_\sigma}{kT} \right)^2 + \frac{1}{75} \left( \frac{\chi_\sigma}{kT} \right)^4 + \frac{29}{55125} \left( \frac{\chi_\sigma}{kT} \right)^6 + \dots \right\}.$$

It will be noticed that the virial term independent of  $T$  is absent. At sufficiently high temperatures the relation approximates to

$$pv = RT + \frac{RTb}{v} - \frac{N^2 b \chi_\sigma^2}{3RTv}.$$

Thus the attraction virial tends to disappear as the temperature is raised. The explanation of this is indicated as follows.

The potential of a molecule in the field of another is exactly reversed in sign by turning its axis through two right angles. At high temperatures there are very nearly equal numbers of pairs of molecules orientated in the two kind of ways, so that the two sets neutralize each other's effect on the attraction virial. When there is no such balancing effect the virial term independent of  $T$  will exist.

#### *The Second Virial Coefficient of a Binary Mixture of Gases.*

It is impossible to calculate the virial coefficient  $B$  for a mixture of two gases from the values of the coefficients  $B_1$  and  $B_2$  of the separate gases. The interaction of the two unlike molecules introduces a new factor.

Suppose that there are  $\nu_1$  molecules of the gas 1 and  $\nu_2$  molecules of the gas 2 in a vessel of unit volume. Let  $\nu_{01}$  and  $\nu_{02}$  be the concentrations of molecules of gas 1 and 2 respectively outside the field of any other molecule. Then it is evident from the previous deductions that

$$\nu_{01} = 1 - f_1(\nu_1, \nu_2, T), \quad \nu_{02} = 1 - f_2(\nu_1, \nu_2, T).$$

\* Keesom, *loc. cit.* p. 271.

In these expressions

$$f_1(\nu_1, \nu_2, T) = \int (1 - e^{-\chi_1 kT}) d\omega dv,$$

$$f_2(\nu_1, \nu_2, T) = \int (1 - e^{-\chi_2 kT}) d\omega dv,$$

the integrations being taken for all positions and orientations of a molecule of gas 1 and 2 respectively over all the fields due to the other molecules in their actual positions at any given instant.  $\chi_1$  and  $\chi_2$  are the potentials of the molecule of gas 1 and of gas 2 in the instantaneous field due to the other molecules.

If  $C$  is the total gram molecular concentration of the mixture, and  $n_1$  and  $n_2$  are the molecular fractions of the two gases, then the quantities

$$A_1 = \frac{n_1 C}{1 - f_1(\nu_1, \nu_2, T)}, \quad A_2 = \frac{n_2 C}{1 - f_2(\nu_1, \nu_2, T)},$$

are the activities of the two gases in the mixture. It may be readily shown that

$$dp/C = RTn_1 d \log A_1 + RTn_2 d \log A_2. \quad (g)$$

If the simultaneous approach of three or more molecules be neglected, then

$$f_1(\nu_1, \nu_2, T) = \nu_1 \phi_1(T) + \nu_2 \phi_{12}(T),$$

$$f_2(\nu_1, \nu_2, T) = \nu_2 \phi_2(T) + \nu_1 \phi_{21}(T).$$

In these expressions

$$\phi_1(T) = \int (1 - e^{-\chi kT}) d\omega dv,$$

the integration being taken for all positions and orientations of a molecule of gas 1 over the entire field of a molecule of gas 1;  $\phi_2(T)$  is the corresponding quantity for a molecule of gas 2 in the field of a molecule of gas 2; and  $\phi_{12}(T)$  for a molecule of gas 1 in the field of a molecule of gas 2. It is evident that  $\phi_{12}(T) = \phi_{21}(T)$ . Thus

$$A_1 = \frac{n_1 C}{1 - C \{ n_1 \Phi_1(T) + n_2 \Phi_{12}(T) \}},$$

$$A_2 = \frac{n_2 C}{1 - C \{ n_2 \Phi_2(T) + n_1 \Phi_{12}(T) \}}.$$

If these values be substituted in (g) we obtain to the required degree of approximation

$$pv = RT + RT \left\{ \frac{n_1^2 \Phi_1(T) + 2n_1 n_2 \Phi_{12}(T) + n_2^2 \Phi_2(T)}{2v} \right\},$$

in which  $v$  is written for  $1/C$ .

As a corollary of this it follows that for gases that are not too concentrated, so that the third virial coefficient may be neglected, if  $n_1$  gram molecules of a gas 1 occupying a volume  $v$  exert a pressure  $p_1$ ; and if  $n_2$  gram molecules of a gas 2 occupying the same volume exert a pressure  $p_2$ ; then when both these quantities of gas together occupy the volume  $v$  they will exert a pressure equal to  $p_1 + p_2 + \Delta p$ , where

$$\Delta p = RT \frac{n_1 n_2 \Phi_{12}(T)}{v^2}.$$

Such experiments as have been performed on the volume pressure relation of binary mixtures have mostly been carried out at high pressures. While such experiments may afford valuable qualitative evidence, yet any deduction from them of an exact nature concerning the interaction between the unlike molecules is very difficult.

It is sometimes considered advantageous to use high concentrations, because it is supposed that thereby the molecules are made to approach each other more nearly and so produce forces which otherwise would not be exerted. So long, however, as the temperature is not raised the molecules do not approach each other more nearly but only more frequently. Therefore, although the effect to be measured is larger, nothing essentially new is obtained by the use of higher pressures, except the influence of multiple encounters, which from the present point of view should be looked upon as a disadvantageous complication.

On the other hand, careful differential measurements made at moderate pressures have the great advantage of yielding to the simple mathematical treatment given above. In order to deduce the real nature of the interaction it is necessary that measurements be made not only at one temperature but at several over a fairly wide range. If this were done interesting results as to the "collision volume" of, for example, a monatomic molecule and a complex one could be deduced, and also something concerning the forces between them.

Chemical Department,  
The University, Manchester,  
May 1923.

XXVII. *On the Lateral Vibrations of Rods of Variable Cross-section.* By DOROTHY M. WRINCH, D.Sc., Fellow of Girton College, Cambridge, and Member of the Research Staff, University College, London\*.

IN a preceding paper †, the lateral vibrations of a thin conical bar with a free tip and various conditions of support at its base were discussed, mainly from the point of view of the nodal arrangement associated with the various tones. The object of the present paper is to extend this investigation to thin bars of certain other very general types.

If a bar has a cross-section of area  $\omega$  at a distance  $w$  from its tip, and if the section has a radius of gyration  $k$  about a central axis in its plane perpendicular to the lateral displacement, the equation of motion is known to be ‡

$$\frac{\partial^2}{\partial w^2} E\omega k^2 \frac{\partial^2 y}{\partial t^2} + \omega \rho \frac{\partial^2 y}{\partial t^2} = 0,$$

where  $y$  is the lateral displacement and  $E, \rho$  are respectively Young's modulus and the density of the bar, it being assumed that the rotary inertia of the bar § may be neglected. We will assume that a longitudinal section of the bar which cuts any one cross-section in a line which is a principal axis of that section cuts every other cross-section in lines which are principal axes of those sections, and we will discuss only those vibrations in which the displacement is in a direction perpendicular to a set of principal axes of the cross-sections. As we pass from section to section,  $\omega$  and  $k$  both vary and are functions of the distance of the section from the tip of the bar.

The cases of practical interest which arise all appear to be included in the class of problems for which  $\omega$  and  $k$  are proportional to powers of the distance from the tip. If we write

$$\omega = Aw^{2\lambda}, \quad k^2 = Bw^{2\mu},$$

where  $A$  and  $B$  are constants, the differential equation becomes

$$\frac{\partial^2}{\partial w^2} w^{2\lambda+2\mu} \frac{\partial^2 y}{\partial w^2} = - \frac{\rho}{EB} w^{2\lambda} \frac{\partial^2 y}{\partial t^2} :$$

on this occasion, for reasons which will appear subsequently, we will consider only those cases in which  $\mu < 2$ .

\* Communicated by the Author.

† Proc. Roy. Soc. A. vol. ci. pp. 493-508 (1922).

‡ Kirchhoff, *Sitz. der Akad. zu Berlin*, 1879, p. 815.

§ Rayleigh, 'Theory of Sound,' vol. i. p. 286.

For a periodic motion, of period  $\frac{2\pi}{p}$ , the equation becomes

$$\frac{\partial^2}{\partial w^2} w^{2\lambda+2\mu} \frac{\partial^2 y}{\partial t^2} = \frac{\rho I^2}{EB} w^{2\lambda} y,$$

and the values of  $p$  will be determined from this equation together with the conditions at the ends of the bar. If  $k'$  be the radius of gyration about another central axis in the cross-sections, the equation of motion when the displacement  $y$  is in a direction perpendicular to this axis is

$$\frac{\partial^2}{\partial w^2} w^{2\lambda+2\mu'} \frac{\partial^2 y}{\partial t^2} = \frac{\rho I'^2}{EB'} w^{2\lambda} y, \quad \text{if } k'^2 = B' w^{2\mu'},$$

and this equation and the conditions at the ends of the bar will give the periods of this set of vibrations. In general, when  $\mu$  and  $\mu'$  are not equal, each type of oscillation will possess its own set of periods and its own characteristic nodal arrangement associated with the various periods. It will be sufficient to investigate the characteristics of the vibrations associated with one radius of gyration, say that to which the index  $\mu$  applies.

As an example of the type of bar to which the analysis is applicable, we may cite the case of a bar which has an elliptic cross-section with axes  $a$  and  $a'$ , such that

$$a = Aw^\mu, \quad a' = A'w^{\mu'}.$$

The area of the cross-section at a distance  $w$  from the tip will be proportional to  $w^{\mu+\mu'}$ , and the principal radii of gyration are given by

$$k^2 = \frac{A^2}{4} w^{2\mu}, \quad k'^2 = \frac{A'^2}{4} w^{2\mu'},$$

and  $\omega$  will be proportional to  $w^{\mu+\mu'}$ . Inserting these values in the general equation, we shall obtain the two equations of motion.

### *The Characteristic Equation of Motion.*

If we introduce a new variable  $z$ , defined by the relations

$$z = qw, \quad q^{4-2\mu} = \frac{\rho I^2}{EB},$$

the equation of motion becomes

$$\frac{\partial^2}{\partial z^2} z^{2\lambda+2\mu} \frac{\partial^2 y}{\partial t^2} = z^{2\lambda} y.$$

With the use of the operator

$$\mathfrak{D}_z = z \frac{\partial}{\partial z},$$

we may write the equation in the form

$$\mathfrak{D}(\mathfrak{D}-1)z^{2\lambda+2\mu-2}\mathfrak{D}(\mathfrak{D}-1)y = z^{2\lambda+2\mu}y.$$

$$\text{or } (\mathfrak{D}+2\lambda+2\mu-2)(\mathfrak{D}+2\lambda+2\mu-3)\mathfrak{D}(\mathfrak{D}-1)y = z^{2\lambda+2\mu}y.$$

It will evidently be convenient to make the substitutions

$$s = \frac{2}{2-\mu}, \quad x = sz^{1/s}, \quad \mathfrak{D}_z = s\mathfrak{D}_s,$$

for the equation then becomes

$$\mathfrak{D}(\mathfrak{D}+4a_1)(\mathfrak{D}+4a_2)(\mathfrak{D}+4a_3)y = x^2y,$$

where

$$4a_1, 4a_2, 4a_3 = -s, s(2\lambda+2\mu-2), s(2\lambda+2\mu-3).$$

This equation is the *characteristic equation* in its most convenient form. Since we are considering only those cases in which  $\mu < 2$ ,  $s$  is positive, and the tip of the bar is therefore given by

$$z = x = 0.$$

We will take the bar to be of unit length. Then the base is given by

$$z = q, \quad x = sq^{1/s}.$$

### Series Solutions of the Characteristic Equation.

There are, in general, four series solutions of the characteristic equation. They are series of hypergeometric type with four denominators\*. The general form for the displacement is, in fact, in general

$$y = Ay + A_1y_1 + A_2y_2 + A_3y_3,$$

where  $A, A_1, A_2, A_3$  are constants determined by the conditions of support, and

$$\begin{aligned} y &= F(x^4/4^4; a_1, a_2, a_3) \\ &= 1 + \frac{(x/4)^4}{1!(1+a_1)(1+a_2)(1+a_3)} \\ &\quad + \frac{(x/4)^8}{2!(1+a_1)(2+a_1)(1+a_2)(2+a_2)(1+a_3)(2+a_3)} + \dots \end{aligned}$$

$$y_1 = x^{-4a_1}F(x^4/4^4; -a_1, a_2-a_1, a_3-a_1),$$

$$y_2 = x^{-4a_2}F(x^4/4^4; -a_2, a_3-a_2, a_1-a_2),$$

$$y_3 = x^{-4a_3}F(x^4/4^4; -a_3, a_1-a_3, a_2-a_3).$$

\* Cp. Phil. Mag. vol. xlv. pp. 818-827 (1923).



In the present investigation we are concerned only with the case of a bar vibrating with its tip free. In all cases, therefore, the expression for the displacement must be such as to ensure that the shearing stress and bending moment vanish at  $x=0$ . These are proportional respectively to

$$z^{2\lambda+2\mu} \frac{\partial^2 y}{\partial z^2}, \quad \frac{\partial}{\partial z} z^{2\lambda+2\mu} \frac{\partial^2 y}{\partial z^2}.$$

Now, the terms making up the bending moment begin with multiples of  $z^\alpha$ , where for  $y, y_1, y_2, y_3$  respectively  $\alpha$  is given by

$$2\lambda + 2\mu - 3, \quad 2\lambda + 2\mu - 3 - 4a_1/s, \quad 2\lambda + 2\mu - 3 - 4a_2/s,$$

Since 
$$2\lambda + 2\mu - 3 - 4a_3/s.$$

$4a_1/s = -1, \quad 4a_2/s = 2\lambda + 2\mu - 2, \quad 4a_3/s = 2\lambda + 2\mu - 3,$   
these powers of  $z$  are, respectively,

$$2\lambda + 2\mu - 3, \quad 2\lambda + 2\mu - 2, \quad -1, 0.$$

In order that the shearing stress and bending moment may vanish at  $x=z=0$ , it is necessary that  $\alpha$  should be positive in each case. For  $y_2$  and  $y_3$ ,  $\alpha$  has the values  $-1$  and  $0$  respectively. Therefore the expression for the displacement cannot contain the series  $y_2$  and  $y_3$ . Thus the displacement takes the form

$$y = Ay + A_1 y_1.$$

#### *The Rod with clamped base.*

If the base of the rod is clamped, the equations

$$y = Ay + A_1 y_1 = 0,$$

$$dy/dz = A dy/dz + A_1 dy_1/dz = 0$$

must be satisfied at the point

$$z = q, \quad x = sq^{1/s}.$$

If, therefore,  $u$ , a function of  $x$  be defined by the relation

$$u = y \partial y_1 / \partial z - y_1 \partial y / \partial z,$$

in view of the fact that

$$p = \sqrt{\frac{EB}{\rho}} q^{2/s},$$

the periods associated with the first, second, third, ...  $r$ th tones are given by

$$\frac{2\pi}{p} = 2\pi \sqrt{\frac{\rho}{EB}} \cdot \left(\frac{b_r}{s}\right)^{-2},$$

where  $b_1, b_2, \dots, b_r, \dots$  are the roots in order of magnitude of the equation

$$u(x) = 0.$$

We proceed to find the linear differential equation satisfied by the function  $u(x)$ .

Writing  $P=y_1$ ,  $Q=y$ , we have

$$u = \frac{dP}{dz} Q - \frac{dQ}{dz} P = P'Q - Q'P,$$

and  $P$  and  $Q$  are two solutions of the equation

$$\frac{\partial^2}{\partial z^2} z^{2m} \frac{\partial^2 y}{\partial z^2} = z^{2\lambda} y \quad (m = \lambda + \mu),$$

which may also be written

$$z^4 y^{iv} + 4mz^3 y^{iii} + 2m(2m-1)z^2 y^{ii} = z^{4+\mu} y. \quad (1)$$

It will be convenient to introduce the notation, after Nicholson\*,

$$P_s Q_r = \frac{d^r Q}{dz^r} \cdot \frac{d^s P}{dz^s} - \frac{d^r P}{dz^r} \cdot \frac{d^s Q}{dz^s}.$$

Then

$$P_1 Q = u \quad (2)$$

and

$$z^4 P_4 Q + 4mz^3 P_3 Q + 2m(2m-1)z^2 P_2 Q = 0, \quad (3)$$

$$z^4 P_4 Q_1 + 4mz^3 P_3 Q_1 + 2m(2m-1)z^2 P_2 Q_1 = z^{4+\mu} \mu, \quad (4)$$

$$z^4 P_4 Q_2 + 4mz^3 P_3 Q_2 = z^{4+\mu} P Q_2, \quad (5)$$

and evidently

$$P_r Q_r = 0.$$

Differentiating the equation (2) three times, we find

$$P_2 Q = \frac{1}{z} \mathfrak{S} u, \quad (6)$$

$$P_3 Q + P_2 Q_1 = \frac{1}{z^2} \mathfrak{S}(\mathfrak{S}-1) u, \quad (7)$$

$$P_4 Q + 2P_3 Q_1 = \frac{1}{z^3} \mathfrak{S}(\mathfrak{S}-1)(\mathfrak{S}-2) u. \quad (8)$$

\* Proc. Roy. Soc. A. vol. xcvi. p. 506 (1917).

Eliminating  $P_4Q$  by means of the equations (3) and (8), we have

$$2P_3Q_1 - \frac{4m}{z} P_3Q = \frac{1}{z^3} \mathfrak{S} \{ (\mathfrak{S}-1)(\mathfrak{S}-2) + 2m(2m-1) \} u,$$

and eliminating  $P_3Q$  by means of (7) we obtain

$$\begin{aligned} 2P_3Q_1 + \frac{4m}{z} P_2Q_1 &= \frac{1}{z^3} \mathfrak{S} \{ (\mathfrak{S}-1)(\mathfrak{S}-2) + 4m(\mathfrak{S}-1) \\ &\quad + 2m(2m-1) \} u \\ &= \frac{1}{z^3} \mathfrak{S}(\mathfrak{S}+2m-1)(\mathfrak{S}+2m-2)u. \quad (9) \end{aligned}$$

Differentiating (9) we find that

$$\begin{aligned} 2P_4Q_1 + 2P_3Q_1 - \frac{4m}{z^2} P_2Q_1 + \frac{4m}{z} P_3Q_1 \\ = \frac{1}{z^4} \mathfrak{S}(\mathfrak{S}-3)(\mathfrak{S}+2m-1)(\mathfrak{S}+2m-2)u, \end{aligned}$$

and this result combined with the equation (4) becomes

$$\begin{aligned} 2z^4P_3Q_2 - 4mz^3P_3Q_1 - 8m^2z^2P_2Q_1 \\ = \mathfrak{S}(\mathfrak{S}-3)(\mathfrak{S}+2m-1)(\mathfrak{S}+2m-2)u + 2z^4u. \end{aligned}$$

Taken in conjunction with (9) it may be written

$$2z^4P_3Q_2 = \{ \mathfrak{S}(\mathfrak{S}+2m-1)(\mathfrak{S}+2m-2)(\mathfrak{S}+2m-3) + 2z^4 \} u. \quad (10)$$

A further differentiation yields the result

$$2P_4Q_2 = \frac{1}{z^5} \{ \mathfrak{S}(\mathfrak{S}-4)(\mathfrak{S}+2m-2) \} u.$$

If we combine this equation with the equation (10) the result is

$$\begin{aligned} (\mathfrak{S}+2m-1)(\mathfrak{S}+2m-2)(\mathfrak{S}+2m-3)(\mathfrak{S}+4m-4)u \\ + 4z^4(\mathfrak{S}+m+\lambda)u = 0, \quad (11) \end{aligned}$$

a linear differential equation of the fifth order for the function  $u(x)$ .

To obtain the solution of this equation, we may consider the equation

$$\mathfrak{S}(\mathfrak{S}+\alpha_1)(\mathfrak{S}+\alpha_2)(\mathfrak{S}+\alpha_3)(\mathfrak{S}+\alpha_4)y = z(\mathfrak{S}+1+\alpha)y. \quad (12)$$

One solution is evidently

$$y = F(z; \alpha; \alpha_1, \alpha_2, \alpha_3, \alpha_4) \\ = 1 + \frac{(1+\alpha)z}{1!(1+\alpha_1)(1+\alpha_2)(1+\alpha_3)(1+\alpha_4)} + \dots$$

Next, if we write

$$y = z^{-\alpha_1} Y, \quad \mathfrak{D}y = z^{-\alpha_1} (\mathfrak{D} - \alpha_1) Y,$$

the equation for  $Y$  is

$$(\mathfrak{D} - \alpha_1) \mathfrak{D} (\mathfrak{D} + \alpha_2 - \alpha_1) (\mathfrak{D} + \alpha_3 - \alpha_1) Y = z (\mathfrak{D} + 1 + \alpha - \alpha_1) Y.$$

and one solution is evidently

$$Y = F(z; \alpha - \alpha_1; \alpha_2 - \alpha_1, \alpha_3 - \alpha_1, \alpha_4 - \alpha_1, -\alpha_1).$$

Therefore, another solution of the equation for  $y$  is

$$y_1 = z^{-\alpha_1} F(z; \alpha - \alpha_1; \alpha_2 - \alpha_1, \alpha_3 - \alpha_1, \alpha_4 - \alpha_1, -\alpha_1).$$

The symmetry of the equation in  $\alpha_1, \alpha_2$ , and  $\alpha_3$  at once shows that the remaining solutions are

$$y_2 = z^{-\alpha_2} F(z; \alpha - \alpha_2; \alpha_3 - \alpha_2, \alpha_4 - \alpha_2, \alpha_1 - \alpha_2, -\alpha_2),$$

$$y_3 = z^{-\alpha_3} F(z; \alpha - \alpha_3; \alpha_4 - \alpha_3, \alpha_1 - \alpha_3, \alpha_2 - \alpha_3, -\alpha_3),$$

$$y_4 = z^{-\alpha_4} F(z; \alpha - \alpha_4; \alpha_1 - \alpha_4, \alpha_2 - \alpha_4, \alpha_3 - \alpha_4, -\alpha_4).$$

If we write

$$x = kz^{4/s}, \quad k = 4 \left( \frac{s}{4} \right)^4,$$

the period equation will become

$$\mathfrak{D}_x (\mathfrak{D}_x + \alpha_1) (\mathfrak{D}_x + \alpha_2) (\mathfrak{D}_x + \alpha_3) (\mathfrak{D}_x + \alpha_4) y = -x (\mathfrak{D}_x + 1 + \alpha) y,$$

where

$$\alpha_1, \alpha_2, \alpha_3, \alpha_4; \alpha = \frac{s}{4} (2m-1), \frac{s}{4} (2m-2), \frac{s}{4} (2m-3),$$

$$\frac{s}{4} (4m-4); \frac{s}{4} (m+\lambda) - 1$$

$$= k + \frac{s}{4}, k, k - \frac{s}{4}, 2k, k - \frac{1}{2},$$

with

$$k = \frac{s}{4} (m-1).$$

The series solutions of the period equation are therefore

of hypergeometric type with five denominators and one numerator and may be written in the form

$$y = z^\beta F\left(-4\left(\frac{sz^{1/4}}{4}\right)^4; c; d_1, d_2, d_3, d_4\right),$$

with various values of the parameters  $\beta, c, d_1, d_2, d_3, d_4$ . Of these various solutions one is proportional to the function  $u(x)$ . To discover which solution it is which has this property, we remark that the function  $u$  begins with a term independent of  $z$ . Hence, the function  $u$  will be a multiple of the series in which  $\beta = 0$ . This is evidently the series

$$F\left(-4\left(\frac{sz^{1/4}}{4}\right)^4; \alpha; \alpha_1, \alpha_2, \alpha_3, \alpha_4\right).$$

The period equation therefore takes the form

$$F\left(-4\left(\frac{x}{4}\right)^4; \alpha; \alpha_1, \alpha_2, \alpha_3, \alpha_4\right) = 0, \quad \dots \quad (13)$$

and the periods are given by

$$\frac{2\pi}{p} = 2\pi \sqrt{\frac{\rho}{BE}} \left(\frac{b_r}{s}\right)^{-2},$$

where  $b_1, b_2, b_3 \dots b_r \dots$  are the roots of this equation in order of magnitude.

*The Roots of the Period Equation for the Rod with  
clamped base.*

The roots of the equation (13) may be found by means of the asymptotic expansion of the hypergeometric function in question. The numerical discussion for special values of the parameters of the successive roots, which alone has been attempted by previous writers, throws no light on the general characteristics of the roots. Employing the asymptotic expansion\*, we obtain an approximation to the roots in the form

$$\begin{aligned} b_r &= \gamma_r + \frac{\nu_1}{2\gamma_r} \\ \text{if} \quad \gamma_r &= \frac{\pi}{4} \sigma + (r - \tfrac{1}{2})\pi, \\ \sigma &= \alpha_1 + \alpha_2 + \alpha_3 + \alpha_4 - \alpha + 3/2, \end{aligned}$$

the terms of order  $1/\gamma_r^2$  being neglected.

\* Cf. a paper by the present writer, Phil. Mag. vol. xlv. pp. 818-827 (1923).

In this expression,

$$\nu_1 = \frac{1}{4}(\Sigma_2 + 6\Sigma_1 + 25),$$

where  $\Sigma_n$  denotes the sum of the products  $n$  at a time of the five quantities

$$-\sigma, \quad 4\alpha_1 - \sigma, \quad 4\alpha_2 - \sigma, \quad 4\alpha_3 - \sigma, \quad 4\alpha_4 - \sigma.$$

Since

$$\alpha_1, \alpha_2, \alpha_3, \alpha_4 = k \pm \frac{s}{2}, \quad k, \quad 2k,$$

the five quantities involved are

$$-4k-2, \quad s-2, \quad -2, \quad -s-2, \quad 4k-2,$$

and we deduce at once that  $\Sigma_1 = -10$ , and owing to the symmetric nature of the values of the parameters,

$$\begin{aligned} \Sigma_2 &= -(4k+2)(4k-2) - (s-2)(s+2) + 32 \\ &= 40 - 16k^2 - s^2. \end{aligned}$$

Therefore

$$\nu_1 = \frac{1}{4}(5 - 16k^2 - s^2),$$

$$\gamma_r = \pi(k+r),$$

and the approximation takes the convenient form

$$b_r = \gamma_r + \frac{1}{4}(5 - 16k^2 - s^2) / 2\gamma_r$$

if terms of order  $1/\gamma_r^2$  are neglected. Thus the periods for the free-clamped bar are given by

$$\frac{2\pi}{p} = 2\pi \sqrt{\left(\frac{\rho}{BE}\right) s^2 (\gamma_r + (5 - 16k^2 - s^2) / 8\gamma_r)^{-2}},$$

terms of order  $1/\gamma_r^2$  being neglected. The periods are therefore expressed in terms of two parameters, which may be called indices for the bar. Now the bar was specified by the conditions

$$\omega = A u^{2\lambda}, \quad k^2 = B u^{2\mu}$$

and

$$s = 2/(2-\mu), \quad k = \frac{s}{2}(\lambda + \mu - 1).$$

Evidently, then, the value of  $A$  is quite irrelevant to the periods of the bar, whatever the conditions of support. Thus, for example, all conical rods, which have the same indices  $s, k$ , will have the same periods if the value of the

constant  $\frac{\rho}{BE}$  is the same for all the rods. Further, neither A nor B, nor the particular values of E and  $\rho$  for the bar is relevant to the ratios of the periods.

*The Nodal Equation.*

The displacement at any point of the bar is given by

$$y = Ay + A_1y_1.$$

Owing to the fact that the base of the bar is clamped,

$$0' = Ay + A_1y_1,$$

when  $x$  has any of the values

$$b_1, \quad b_2, \quad \dots b_r \dots$$

The nodal equation for the  $r$ th tone is therefore

$$\frac{y(x)}{y_1(x)} = \frac{y(b_r)}{y_1(b_r)}.$$

Let

$${}_1b_r, \quad {}_2b_r, \quad \dots {}_mb_r \dots, \quad {}_rb_r (= b_r),$$

be the roots of this equation in order of magnitude. Then the distance of the  $m$ th node in the  $r$ th tone from the tip (the length of the bar being unity) is given by

$${}_mN_r = ({}_mb_r)^r.$$

It will be convenient to call these quantities "nodal lengths" and in particular to call  ${}_mN_r$  "the  $m$ th nodal length associated with the  $r$ th tone."

The problem of finding the roots of the nodal equation is similar, in some respects, to the problem of finding the roots of the period equation. For, we want to find the whole sequence of roots for which  $x \leq b_r$ , and in the  $r$ th tone there will, of course, be  $r$  of them. Any method which yields the roots one at a time is useless for the purpose of obtaining information about the nodal arrangement which, rather than the accurate determination of a few of the nodal distances associated with the very early tones, is our aim in the present communication. For our purposes, it is plainly more important to use a method which locates the roots of the nodal equation within certain limits than to adopt a procedure which will yield only one root at a time, even if it locates these individual roots to a higher degree of accuracy.

*Other Solutions of the Characteristic Equation of Motion.*

If we are to investigate the roots of an equation of type

$$\frac{P(x)}{Q(x)} = \frac{P(b)}{Q(b)}$$

by the employment of the asymptotic expansions of the functions, it is evident that it will be desirable that the orders of magnitude of  $P$  and  $Q$  for large values of  $x$  shall be as different as possible. We obtained a nodal equation of this form with

$$P = y_1, \quad Q = y.$$

But it is evident that we are not limited to this determination of  $P$  and  $Q$ . We had the equation

$$y = Ay + A_1y_1,$$

but this equation might be written in the form

$$y = CY_1 + DY,$$

where  $Y$  and  $Y_1$  are linear combinations of  $y$  and  $y_1$ , and therefore satisfy the original characteristic equation of motion. The only proviso, namely, that the bending moment and shearing stress shall vanish at the free tip, is evidently satisfied if  $Y$  and  $Y_1$  are *any* linear combinations of  $y$  and  $y_1$  whatever. Thus we may take a new form for the displacement

$$y = CY + D_1Y_1,$$

and the conditions at the base will yield the fact that at  $x=b$ ,

$$CY + D_1Y_1 = 0,$$

$$C \frac{dY}{dz} + D_1 \frac{dY_1}{dz} = 0.$$

From these equations we can, of course, obtain the period equation in the form

$$Y_1 \frac{dY}{dz} - Y \frac{dY_1}{dz} = 0.$$

This form can be shown to yield the standard form of the period equation given in (13), since  $Y$  and  $Y_1$  equally with  $y$  and  $y_1$  are solutions of the characteristic equation of motion.



The equations yield the nodal equation in the form

$$\frac{Y(x)}{Y_1(x)} = \frac{Y(b_r)}{Y_1(b_r)},$$

and we proceed now to consider the most advantageous choice of  $Y$  and  $Y_1$ , not with the view of obtaining convenient convergent expansions for small values of  $x$ , but with the express purpose of obtaining functions whose asymptotic behaviour when  $x$  is large is convenient for the solution of the equation

$$\frac{Y}{Y_1}(x) = \frac{Y}{Y_1}(b_r). \quad . \quad . \quad . \quad . \quad (14)$$

Now the characteristic equation of motion,

$$\mathfrak{S}(\mathfrak{S} + 4a_1)(\mathfrak{S} + 4a_2)(\mathfrak{S} + 4a_3)y = x^4 y,$$

is well known to have four types of asymptotic expansion of its solutions, namely,

$$\mathcal{Y}(a_1, a_2, a_3) = e^x x^{-\sigma} \left\{ 1 + \frac{\alpha_1}{x} + \dots \right\},$$

$$\begin{aligned} \mathcal{Y}_1(a_1, a_2, a_3) = x^{-\sigma} \left\{ \cos\left(x - \frac{\pi\sigma}{2}\right) \right. \\ \left. + \frac{\alpha_1}{x} \cos\left(x - \frac{\pi}{2}(\sigma+1)\right) + \dots \right\}, \end{aligned}$$

$$\begin{aligned} \mathcal{Y}_2(a_1, a_2, a_3) = x^{-\sigma} \left\{ \sin\left(x - \frac{\pi\sigma}{2}\right) \right. \\ \left. + \frac{\alpha_1}{x} \sin\left(x - \frac{\pi}{2}(\sigma+1)\right) + \dots \right\}, \end{aligned}$$

$$\mathcal{Y}_3(a_1, a_2, a_3) = e^{-x} x^{-\sigma} \left\{ 1 - \frac{\alpha_1}{x} + \dots \right\},$$

where

$$\sigma = a_1 + a_2 + a_3 + 3/2 = 4k + 3/2,$$

and  $\alpha_1, \alpha_2 \dots$  are functions of the parameters  $a_1, a_2, a_3$ .

With a view to obtaining, in a simple manner, the distribution of roots of the equation (14), it would evidently be most convenient if one of the two functions  $Y$  and  $Y_1$  contained in its asymptotic expansion and the other did not contain the series  $\mathcal{Y}$ , for then the relative order of magnitude of  $Y$  and  $Y_1$  would be  $e^{-x}$  at most, and an approximation to the roots could quickly be found.

Now, the relation between the solutions  $y, y_1, y_2, y_3$  and the solutions  $\mathcal{Y}, \mathcal{Y}_1, \mathcal{Y}_2, \mathcal{Y}_3$  is known. In the first place,

$$\frac{y_1 2(2\pi)^{3/2}}{\Gamma(1+a_1) \Gamma(1+a_2) \Gamma(1+a_3)} = \mathcal{Y}(a_1, a_2, a_3) + \mathcal{Y}_1(a_1, a_2, a_3),$$

the series  $\mathcal{Y}_3$ , which is of relative order  $e^{-x}$ , being neglected. Since

$$y_1(a_1, a_2, a_3) = x^{-4a_1} y(a_2 - a_1, a_3 - a_1, -a_1),$$

we have similarly

$$\begin{aligned} & \frac{y_1 2(2\pi)^{3/2}}{\Gamma(1+a_2-a_1) \Gamma(1+a_3-a_1) \Gamma(1-a_1)} \\ &= x^{-4a_1} [\mathcal{Y}(a_2-a_1, a_3-a_1, -a_1) + \mathcal{Y}_1(a_2-a_1, a_3-a_1, -a_1)], \end{aligned}$$

But

$$\mathcal{Y}(a_2-a_1, a_3-a_1, -a_1) = e^x x^{-\tau} \left\{ 1 + \frac{\alpha_1}{x} + \dots \right\},$$

$$\mathcal{Y}_1(a_2-a_1, a_3-a_1, -a_1)$$

$$= x^{-\tau} \left\{ \cos\left(x - \frac{\pi\tau}{2}\right) + \frac{\alpha_1}{x} \cos\left(x - \frac{\pi}{2}(\tau+1)\right) + \dots \right\},$$

where

$$\tau = (a_2 - a_1) + (a_3 - a_1) + (-a_1) + 3/2,$$

just as

$$\sigma = a_1 + a_2 + a_3 + 3/2.$$

Evidently

$$\tau = \sigma - 4a_1.$$

Therefore

$$\begin{aligned} & \frac{y_1 2(2\pi)^{3/2}}{\Gamma(1+a_2-a_1) \Gamma(1+a_3-a_1) \Gamma(1-a_1)} \\ &= \mathcal{Y}(a_1, a_2, a_3) + x^{-\sigma} \left\{ \cos\left(x - \frac{\pi}{2}\sigma + 2\pi a_1\right) \right. \\ & \quad \left. + \frac{\alpha_1}{x} \cos\left(x - \frac{\pi}{2}(\sigma+1) + 2\pi a_1\right) + \dots \right\}. \end{aligned}$$

If, therefore, we choose  $Y$  to be a multiple of

$$\begin{aligned} & \frac{y_1 2(2\pi)^{3/2}}{\Gamma(1+a_2-a_1) \Gamma(1+a_3-a_1) \Gamma(1-a_1)} \\ & - \frac{y 2(2\pi)^{3/2}}{\Gamma(1+a_1) \Gamma(1+a_2) \Gamma(1+a_3)}, \end{aligned}$$

its asymptotic expansion will contain no series in  $e^x$  and will, indeed, be the same multiple of

$$x^{-\sigma} \left\{ \cos \left( x - \frac{\pi}{2} \sigma + 2\pi a_1 \right) + \frac{\alpha_1}{x} \cos \left( x - \frac{\pi}{2} \sigma + 1 + 2\pi a_1 \right) \dots \right. \\ \left. - \left[ \cos \left( x - \frac{\pi}{2} \sigma \right) + \frac{\alpha_1}{x} \cos \left( x - \frac{\pi}{2} \sigma + 1 \right) + \dots \right] \right\},$$

which may also be written in the form

$$-2x^{-\sigma} \sin a_1 \pi \left\{ \sin \left( x - \bar{k} + \frac{3}{4} \pi \right) + \frac{\alpha_1}{x} \sin \left( x - \bar{k} + \frac{5}{4} \pi \right) + \dots \right\},$$

since

$$\sigma/2 - \alpha_1 = k + 3/4.$$

We may conveniently take  $Y_1$  to be equal to

$$\frac{y 2(2\pi)^{3.2}}{\Gamma(1+a_1) \Gamma(1+a_2) \Gamma(1+a_3)},$$

for then its asymptotic expansion will be

$$x^{-\sigma} e^x \left\{ 1 + \frac{\alpha_1}{x} + \dots \right\},$$

terms of relative order  $e^{-x}$  being neglected.

The nodal equation associated with the  $r$ th tone therefore appears in the form

$$e^{-x} \left\{ \sin \left( x - \bar{k} + \frac{3}{4} \pi \right) + \frac{\alpha_1}{x} \sin \left( x - \bar{k} + \frac{5}{4} \pi \right) + \dots \right\} \left( 1 + \frac{\alpha_1}{x} + \dots \right) \\ = f(x) = f(b_r),$$

where  $b_r$  denotes the root of the period equation associated with the  $r$ th tone. We have already obtained the value of  $b_r$  in the case when the base of the bar is clamped, in the form

$$b_r = \pi(r+k) + \frac{1}{8} \frac{5-16k^2-s^2}{\pi(k+r)} + \dots.$$

For any other conditions of support at the base the nodal equation for the  $r$ th tone still takes the form

$$f(x) = c_r,$$

where  $c_r$  is a constant associated with the  $r$ th period; the value of  $c_r$  for any particular conditions can, of course, be

determined by the formation of a period equation when the conditions at the base have been specified.

To obtain a general idea of the roots of the nodal equation for the bar with clamped base, we put

$$x = (m + k - \frac{1}{4})\pi + \epsilon_m,$$

and the equation then becomes

$$e^{-\epsilon_m} \left( \sin \epsilon_m - \frac{2\alpha_1}{(m + k - \frac{1}{4})\pi + \epsilon_m} + \dots \right) = f(h_r) e^{(m+k-\frac{1}{4})\pi}.$$

Now even in the lower tones,  $f(h_r) e^{(m+k-\frac{1}{4})\pi}$  is small in order of magnitude. For instance, in the fifth tone, for the first, second, third, and fourth nodes from the tip (for which  $m$  takes the values 1, 2, 3, 4, and  $r=5$ ) the order of magnitude of  $f(h_r) e^{(m+k-\frac{1}{4})\pi}$  is

$$\begin{aligned} e^{-\frac{1}{4}\pi} &= 1.59 \times 10^{-6}, & e^{-\frac{3}{4}\pi} &= 3.68 \times 10^{-5}, \\ e^{-\frac{5}{4}\pi} &= 8.51 \times 10^{-4}, & e^{-\frac{7}{4}\pi} &= 1.97 \times 10^{-3}, \end{aligned}$$

respectively. Evidently, the higher the node, the more nearly do the roots of the nodal equation approach the roots of the equation

$$f(x) = 0.$$

The solution of the nodal equation associated with any tone can be carried out by successive approximation to any requisite degree of accuracy.

The roots of the equation

$$f(x) = 0$$

can readily be obtained. If  $\rho_m$  be the  $m$ th root in order of magnitude,

$$\rho_m = \delta_m + \frac{\alpha_1}{\delta_m},$$

with

$$\delta_m = \frac{\pi\sigma}{2} - \alpha_1\pi + (m-1)\pi,$$

terms of order  $1/\delta_r^2$  being neglected.

The value of  $\alpha_1$  can easily be obtained owing to the symmetrical nature of the four quantities,

$$-\sigma, \quad 4\alpha_1 - \sigma, \quad 4\alpha_2 - \sigma, \quad 4\alpha_3 - \sigma,$$

which are evidently equal to

$$-2k + \frac{s}{2} - \frac{3}{2}, \quad -2k - \frac{s}{2} - \frac{3}{2}, \quad 2k + \frac{s}{2} - \frac{3}{2}, \quad 2k - \frac{s}{2} - \frac{3}{2}.$$

Thus

$$\Sigma_1 = -6,$$

$$\Sigma_2 = 6\left(\frac{3}{2}\right)^2 - 2\left((2k)^2 + \left(\frac{s}{2}\right)^2\right) = \frac{27}{2} - 8k^2 - \frac{s^2}{2},$$

and, in consequence,

$$\alpha_1 = \frac{1}{8}(5 - 16k^2 - s^2),$$

$$\delta_m = \pi(k + m - \frac{1}{4}),$$

and  $\rho_m$  is given by

$$\rho_m = \pi(k + m - \frac{1}{4}) + \frac{5 - 16k^2 - s^2}{8\pi(k + m - \frac{1}{4})}.$$

*The Nodal Lengths for a free-clamped bar.*

Adopting the approximation discussed above, the nodal lengths are given by

$$m/r = \left(\frac{\rho_m}{b_r}\right)^s, \quad \dots \dots \dots (15)$$

with

$$b_r = \pi(k + r) + \frac{5 - 16k^2 - s^2}{8\pi(k + r)},$$

$$\rho_m = \pi(k + m - \frac{1}{4}) + \frac{5 - 16k^2 - s^2}{8\pi(k + m - \frac{1}{4})}.$$

The first approximation yielded by this result takes the exceedingly simple form

$$m/r = \left(\frac{k + m - \frac{1}{4}}{k + r}\right)^s,$$

and it is interesting to compare this result, which is in a very convenient shape for practical applications, with results in some particular case which are known to a high degree of accuracy. An obvious case, on which to test our result, is the case of a bar of uniform cross-section vibrating with free tip and clamped base. Seebeck\* gives the nodal lengths for the  $r$ th tone as

$$(.3405, 1.2455, 2.25, 3.25, 4.25 \dots)$$

$$r - 3 + \frac{1}{4} - .0044, \quad r - 2 + \frac{1}{4} + .0002, \quad r - \frac{1}{2} / (r - \frac{1}{2}).$$

\* *Abh. Math. Phys. Classe d. k. Sachs. Gesellschaft d. Wissenschaften*, Leipzig, 1852.

Our approximation becomes (since for a uniform bar  $\lambda = \mu = 0$ ,  $s = 1$ ,  $k = -\frac{1}{2}$ ),

$$(1, 1\frac{1}{4}, 2\frac{1}{4}, 3\frac{1}{4}, 4\frac{1}{4}, \dots, r-3+\frac{1}{4}, r-2+\frac{1}{4}) / (r-\frac{1}{2}),$$

and the last term, nominally

$$(r-\frac{3}{4}) / (r-\frac{1}{2}),$$

must evidently be replaced by unity since the bar is clamped at the base and so has a node there.

The expressions for the nodal ratios associated with a free-clamped bar are independent of the constants ( $E, \rho, B, A$ ) which are associated with the bar, and depend only on the two indices  $s$  and  $k$ . This fact throws light upon the results obtained by previous investigators in this field. For, evidently, bars which share the same indices will possess the same characteristic arrangement. A conical bar, for example, whether it has an elliptic cross-section or a rectangular cross-section, will possess the same indices, namely,  $s = 1$ ,  $k = 2$ . The work of Kirchhoff\*, which ostensibly deals with the case of a conical bar of circular cross-section, applies, in fact, so far as the nodal arrangement is concerned, to a wider class of cases.

Certain interesting characteristics of the nodal arrangement in a free-clamped bar may be deduced from the results given in (15). For consider the difference between  $_{m+1}p_r$  and  $_m p_r$ . If we neglect terms in

$$(\pi(k+m-\frac{1}{4}))^{-2},$$

this difference is evidently of order

$$(k+r)^{-s}.$$

If, however, we are considering the order of magnitude of this difference, in the case when  $r-m$  is small so that it is not permissible to neglect terms of order

$$(\pi(k+m-\frac{1}{4}))^{-2},$$

the difference is evidently of order

$$(k+r)^{-1},$$

Thus, in the case of sufficiently high tones, the nodes near the tip crowd together at intervals of order  $(k+r)^{-s}$ , whereas the interval between successive nodes is of order  $(k+r)^{-1}$ . Thus, as  $s$  increases the crowding of nodes towards the tip in

\* *Loc. cit.*

the higher tones becomes more pronounced. This result points to the exceptional nature of the case when  $s=0$ , which was already evident in the original form of the equation.

*Other Conditions of Support at the Base.*

Whatever the conditions of support at the base, the fact that the tip of the bar is free involves the consequence that the displacement is given by

$$y = CY + C_1 Y_1.$$

The positions of the nodes in the  $r$ th tone are therefore determined by the roots of the equation

$$\frac{Y_1}{Y}(x) = c_r,$$

$c_r$  being some constant associated with the  $r$ th tone. This fact is independent of the conditions of support at the base and persists whether the bar is clamped free or supported at its base. Now an equation of this type will only have  $r$  roots if  $c_r$  is sufficiently small. Therefore if we consider a high node, the arguments used in the special case when, in fact, the value of  $c_r$  was already known and was indeed given by

$$c_r = \frac{Y_1}{Y}(b_r),$$

apply to the present much wider class of cases, and it is equally satisfactory to adopt the roots of the equation

$$\frac{Y_1}{Y}(x) = 0$$

as approximations to the roots of the equation  $\frac{Y_1}{Y}(x) = c_r$ .

Thus associated with the  $r$ th tone we again have the sequence

$$\rho_1, \rho_2, \dots, \rho_r,$$

defined as before. The nodal ratios could next be obtained from these quantities, if we had obtained the values of the roots of the period equation associated with the particular conditions of support at the base. In the general problem of finding characteristics of the nodal arrangement of a bar with free tip, when no specification is given as to the conditions of support at the base, the nodal lengths themselves are not determinate, but, on the other hand, the ratio of the

nodal lengths associated with any one tone can at once be deduced in the form

$$\frac{1}{(\rho_1)^s} p_r = \frac{2}{(\rho_2)^s} p_r = \frac{m}{(\rho_m)^s} p_r \dots$$

In many cases, this fact gives sufficient information for an arrangement of a sequence of values to be recognized as being the nodal arrangement typical of the vibrations of a bar with free tip and particular indices  $s$  and  $k$ . In particular, in the subset of cases which fall under the general classification of cases in which the tip is free and nothing is known of the conditions of support at the base except that the base is fixed, we can immediately deduce the nodal lengths in the form

$$m p_r = \left( \frac{\rho_m}{\rho_r} \right)^s,$$

for since the bar is at rest at its base there must be a node there.

The general characteristics of the nodal arrangement in the case of a free-clamped bar therefore persist in the case of a bar with free tip and any conditions of support at the base. The nodes still crowd towards the tip, the density of nodes in the neighbourhood of the tip and in the neighbourhood of the base being in the ratio

$$(k+r)^s : (k+r).$$

The above results establish therefore the existence of certain characteristic arrangements of nodes which may be associated with a bar possessing certain indices  $s$  and  $k$  which is vibrating with a free tip.

XXVIII. *The Crystal Structure of various Heusler Alloys by the Use of X-Rays.* By J. F. T. YOUNG, M.A.\*

[Plate IV.]

I. INTRODUCTION.

**A**MONG the problems of atomic structure is that of the origin of the magnetic phenomena which are manifest on every side in the diamagnetic, paramagnetic, or ferromagnetic behaviour of all substances. It is of the utmost importance to determine the seat of the magnetic forces and

\* Communicated by Professor J. C. McLennan, F.R.S.



the cause of their variation in character in the different elements.

For many years the magnetic properties of substances have been ascribed to the action of molecular magnets, but their nature has never been settled. The early theories of magnetism of Weber, Wiedemann, Ampère, and Maxwell, based on analogies to the phenomena of electromagnetic induction, were more or less artificial and far from satisfactory. The advent of the electron theory of matter provided a new view-point, which Langevin and Weiss extended to provide a theory of magnetism which was in qualitative agreement with experience, at least. In their theory the electrons revolving in certain orbits about the nucleus or centre of the atom created magnetic fields, and each electronic current was equivalent to a definite magnetic moment. When an external magnetic field was supposed, it was shown that these magnetic moments were reduced in the direction of the field, producing the diamagnetic modification of the atom. Paramagnetic properties of atoms were explained by assuming that the resultant magnetic moment of the electronic circuits in such an atom was not zero, and the action of the external field was to rotate these atoms so that their magnetic axes would point in the direction of the field as nearly as the thermal reaction towards disorder would allow. Paramagnetism would thus be a function of the strength of the external field, the resultant magnetic moments of the atoms and the demagnetizing effects of thermal agitation, and any attractive forces between the atoms of any other nature. Weiss extended these conceptions to give a plausible explanation of ferromagnetism by introducing the additional hypothesis that the external field called into action an internal "molecular field" which far exceeded in its effect any other forces on the atom and produced large intensities of magnetization. The later developments by Gans\* and Frivold† of these classical theories, and the applications of the quantum theory by Gans‡ and Reiche§ to account for the distribution of energy of rotation of the magneton, all included the hypothesis of an ultimate magnetic unit with a certain magnetic moment, characteristic of the substance, and therefore with a magnetic axis and thus capable of rotation by an external field.

\* R. Gans, *Ann. d. Phys.* xlix. p. 149 (1916); l. p. 163 (1916).

† O. E. Frivold, *Ann. d. Phys.* lxx. p. 1 (1921).

‡ R. Gans, *loc. cit.*

§ F. Reiche, *Ann. d. Phys.* liv. p. 401 (1917).

At first the magnetic particle was supposed to be the atom or molecule, but other attempts have been made, as in Parson's theory of the magneton, and in other hypotheses regarding the structure of the electron, to give a more definite conception. These have been attended with some success in certain directions. However, the molecular theory of magnetism has given the most coherent explanation of such magnetic effects as (1) the effect of mechanical jarring on magnetism, (2) the influence of chemical combination as in salts and the Heusler alloys, (3) the action of temperature variation, and (4) the general mechanical effects included in the term magnetostriction.

The present work was undertaken with a view of testing these theories in the case of Heusler alloys and of determining what, if any, molecular arrangement was related to magnetic phenomena.

The Heusler alloys, discovered in 1903\*, were composed of the paramagnetic metals manganese and aluminium and the diamagnetic metal copper in various proportions, and some were found to have ferromagnetic properties comparable with magnetically soft iron. These alloys must then contain the ultimate ferromagnetic particle. It has been shown definitely that the amount of iron impurity present was quite incapable of producing the effects discovered.

There have been several explanations proposed. Guillaume† applied Faraday's suggestion that chromium and manganese were non-magnetic at ordinary temperatures because their magnetic transformation temperatures were quite low, and put forward the view that the alloying of manganese with aluminium raised the critical temperature so that in the Heusler alloy the manganese had magnetic properties at ordinary temperatures. There has never been decisive experimental evidence to support this theory, although at various times McTaggart and Robertson‡, and later Rhead§, as a result of the microphotographic study of etched specimens, supposed that the ferromagnetism of the alloys was produced in a special allotropic form of manganese dissolved in copper and aluminium.

Heusler himself || built up a theory from the experimental

\* Fr. Heusler, *Ver. de Phys. Ges.* v. p. 219 (1903).

† C. E. Guillaume, *Arch. Sciences Phys. et Nat.* xxiv. p. 381 (1907).

‡ H. A. McTaggart and Robertson, *Proc. Roy. Soc. Can.* (3) ii. p. 31 (1908).

§ E. L. Rhead, *Journ. Inst. of Metals*, (2) iv. p. 89 (1910).

|| Fr. Heusler, *Zeits. anorgan. Chemie*, lxi. p. 277 (1909).

bases that copper and aluminium formed an alloy of composition  $\text{Cu}_3\text{Al}$ , and that copper and manganese formed a series of mixed crystals. In his opinion it was possible for the copper of the compound  $\text{Cu}_3\text{Al}$  to be isomorphously replaced by manganese to form complex compounds of the type,  $\text{Al}_x(\text{MnCu})_{3x}$  or  $\text{Al}_x\text{Cu}_a\text{Mn}_{(3x-a)}$ , which he regarded as the carrier of the ferromagnetic properties. Both formulæ were designed to indicate that maximum ferromagnetic properties were associated with alloys in which the copper and manganese atoms together were three times as plentiful as the aluminium atoms. This conception furnished a ready explanation of the fact that freshly cast alloys were not strongly magnetic, but reached their maximum magnetic properties after artificial "ageing," i.e. prolonged heat treatment at about  $120^\circ\text{C}$ . "Ageing" was represented as the combined action of two simultaneous structural changes, which were identified by a critical study of the variation of magnetic properties with heat treatment. It was shown that either the magnetic moment of the ferromagnetic unit or the number of such units was increased, and at the same time the ability of this unit to rotate freely was more or less reduced. Heusler explained this by saying that at high temperatures the complex compound  $\text{Al}_x\text{Cu}_a\text{Mn}_{(3x-a)}$  was dissociated, but "ageing" gave an opportunity for its formation by association of the constituents. He made the further suggestion that possibly the marked ferromagnetism of the alloys was produced by the individual  $\text{Al}_x\text{Cu}_a\text{Mn}_{(3x-a)}$  molecules which segregated from the solid solution to produce a new crystalline structure.

Various hypotheses have been advanced to explain how ferromagnetic properties could arise in the compound  $\text{Al}_x\text{Cu}_a\text{Mn}_{(3x-a)}$ . Richarz\* thought that new electrons might be set in rotation or their speed and orbital areas changed. Weiss† said that probably the magnetons in the manganese atom were much freer to rotate in the alloy than in the elemental state, while Take‡ ascribed the increased effects with the alloys to an increased magnetic moment per magnetic particle produced by a rearrangement of the electron orbits in the complex molecule. Ross§, however, took a strong position against any of the above theories of the

\* F. Richarz, *Zeits. anorgan. Chemie*, lxi. p. 271 (1909); *Physik. Zeits.* xii. p. 155 (1911).

† P. Weiss, *Jl. de Phys.* (4) vi. p. 689 (1907).

‡ E. Take, *Göttinger Abhandl.* viii. No. 2 (1911).

§ A. D. Ross, *Trans. Faraday Soc.* viii. p. 185 (1912).

Heusler alloys, but believed that the ferromagnetic properties were associated with the occurrence of two inter-metallic compounds  $\text{Cu}_3\text{Al}$  and  $\text{Mn}_3\text{Al}$ , the variation in concentration being the cause of variation in the magnetic properties of the alloys. His objection to Heusler's complex compound  $\text{Al}_x\text{Cu}_a\text{Mn}_{(3x-a)}$  was on the ground that ternary alloys were rare, and a large number of them would be necessary to account for the variation in the quality of the alloys.

In an attempt to distinguish between the above theories and to find some phenomenon which would show a positive variation with magnetic properties, a systematic crystal analysis of definite Heusler alloys in different conditions was undertaken, using X-ray methods.

## II. PREPARATION OF THE ALLOYS.

The samples of Heusler alloys used in the present work were the same ones, the magnetic properties of which were investigated some years ago by McLennan and others\*. They were prepared by melting the constituent metals—copper, manganese, and aluminium, guaranteed chemically pure and free from iron—in a graphite crucible in an ordinary coke furnace, and then casting in moulds. The copper was heated first until it was fluid, and the manganese and aluminium were added in this order to avoid the serious loss of these metals, especially the latter, at high temperatures. A homogeneous alloy was obtained by stirring the molten metals thoroughly with a porcelain rod. The composition of the alloy casting was always very closely given by the amounts of the metals used.

The castings used by the writer were rings which in their final form had the following dimensions: mean radius 3.5 cm., radial thickness 0.6 cm., and width 2.3 cm. Although the alloys were very hard and brittle, it was found possible to machine and grind them to true rings. This not only enabled them to be measured more accurately, but also improved their homogeneity by removing the "skin" of the casting.

The composition of the alloys was known from McLennan's work. The specimens selected for use were:—

Alloy.	Composition.
Alloy IV <i>a</i> ...	15.9 % Al : 23.9 % Mn : 60.3 % Cu.
Alloy III <i>a</i> ...	14.3 % Al : 28.6 % Mn : 57.1 % Cu.

\* J. C. McLennan, Phys. Rev. 1907.

## III. MAGNETIC PROPERTIES OF THE SAMPLES EXAMINED.

The importance of the heat treatment of a Heusler alloy in relation to its magnetic quality has been mentioned already. The history of the "ageing" and other treatment of these alloys by McLennan had been lost in the intervening years, so that with both of them the designation "Condition (1)" shall be taken to mean their magnetic state at the start of this work—*i.e.*, they had been left untouched for fifteen years, during which they had suffered a temperature variation from  $-10^{\circ}\text{C.}$  to  $45^{\circ}\text{C.}$ , due to climatic changes. Their subsequent treatment and magnetic condition is summarized in the following table:—

TABLE I.—Magnetic Properties of Alloys.

Alloy.	Condition.	Treatment.	Magnetic Condition.
IV a ...	(1)	Heat treatment unknown; 15 years' natural "ageing."	$\mu$ max. = 86.8 for A = 7.8 gauss.
IV a ...	(2)	Heated to a bright red— $600^{\circ}\text{C.}$ Quenched in cold water.	$\mu$ max. = 14.6 for H = 8.2 gauss.
III a ...	(1)	Heat treatment unknown; 15 years' natural "ageing."	$\mu$ max. = 1.64 for H = 17.0 gauss.
III a ...	(2)	Heated to a bright red— $600^{\circ}\text{C.}$ Quenched in cold water; then "aged" for 250 hours in an air bath at $110^{\circ}\text{C.}$	$\mu$ max. = 2.54 for H = 18.0 gauss.

The magnetic properties of these various alloys are illustrated by the graphs of fig. 1 and fig. 2, showing the relation between  $\mu$  and H.

The magnetic measurements were made in the standard way with a ballistic galvanometer which was calibrated by a Duddell magnetic standard. The primary circuit wound on the rings consisted of either 50 or 100 turns of No. 18 wire and the secondary circuit of 150 turns of No. 22 wire, both circuits being wound uniformly around the ring. A constant speed reversing switch was used in the primary circuit, and the resulting galvanometer deflexion was converted into lines of magnetic induction, B, from the calibration curve. The magnetizing field, H, was determined from the current and dimensions of the primary circuit.

Between each heat treatment the rings were uncovered, and enough filings taken off to provide samples for the crystal analysis.

Fig. 1.

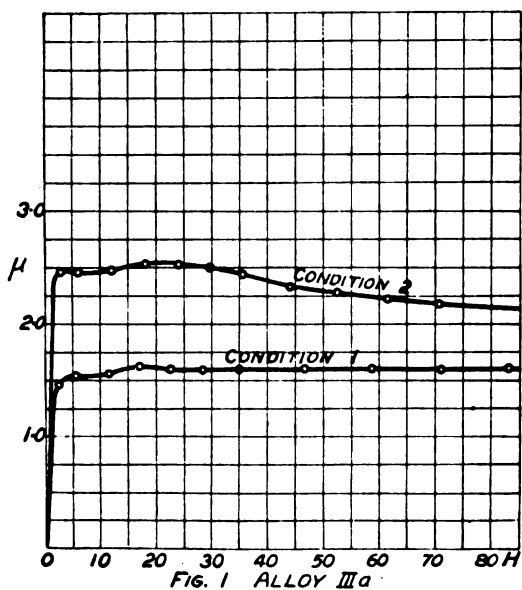
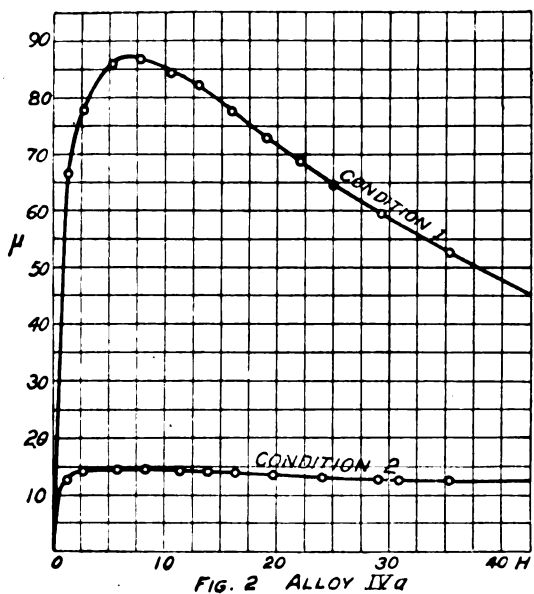


Fig. 2.



## IV. METHOD OF CRYSTAL ANALYSIS.

Since there are no large individual crystals in the Heusler alloys suitable for the Bragg method, the powder method of X-ray analysis was adopted, using a modified form of Hull's arrangement\*. The X-ray tube was a Coolidge water-cooled molybdenum target tube, which could be operated continuously at currents up to 30 milliamperes and 30–40 kilovolts potential. A filter, containing 0.05 gm. of  $ZrO_2$  per sq. cm. with collodion as the binder, was used to absorb wave-lengths other than the  $K\alpha$  doublet, 0.712 Å.U., for which zirconium has a maximum transparency. The monochromatic X-rays then passed through a slit system of lead in the side of the lead box containing the tube, which confined the beam to a width of 2 mm. The crystal powders of aluminium, manganese, and copper and the Heusler alloys were obtained by filing the metals and sifting them through a 200-mesh gauze. The powder was then mounted in the X-ray beam in a paper cylinder of about 0.6 mm. diameter, which was also at the centre of a semicircular brass frame of 11.25 cm. radius, against which was held a strip of Eastman duplitized X-ray film backed by a calcium tungstate intensifying screen. A brass diaphragm divided the film-holder into two parts, so that the diffraction patterns of two substances could be taken simultaneously by filling one-half of the paper tube with one substance and the other half with another. In this way the unknown pattern could be determined in terms of a selected standard. In the case of the heavy metals—manganese and copper and the alloys—it was found necessary to dilute the crystal powder with corn starch, in order to obtain satisfactory diffraction patterns.

The whole apparatus was arranged so that, in addition to taking the photographs of the alloy powders in their natural state, a horseshoe electromagnet with a narrow gap between the poles could be put in position, and diffraction patterns of the alloys taken when in a magnetic field of 3500 gauss. Iron screens were, of course, used to shield the X-ray tube from the stray magnetic field.

## V. RESULTS.

Metallic aluminium was chosen as the standard substance, because it is a constituent of the Heusler alloys; it gives quite intense reflexions from the various crystal planes, and its crystal form and constants have been evaluated several

\* A. W. Hull, *Phys. Rev.* **x.** (6) p. 661 (1917); **xvii.** (5) p. 571 (1921).

times by Hull\*, Scherrer†, and Kirchner‡. The pattern obtained by the writer agreed excellently with the previous solutions of the crystal, viz. that aluminium crystallizes in a face-centred cubic system with the lattice constant,  $d=4.05 \text{ \AA.U.}$  The pattern is shown in No. 1, Pl. IV.

The other constituents of the alloys were then investigated, in order to eliminate any lines which might be due to free metal in the alloy. The comparison method was used throughout the work. The solution of the copper diffraction pattern which is shown in No. 2, Pl. IV., agreed exactly with Bragg's result § from a large crystal, that copper crystallizes in the face-centred cubic system and has a lattice constant,  $d=3.60 \text{ \AA.U.}$

The third metal, manganese, presented great difficulties. Although Groth || has placed manganese in the cubic system, the pattern obtained is much too complex for this to seem probable. All attempts to solve the diffraction pattern of manganese by Hull and Davey's graphical method ¶ failed, and although Runge\*\* and Johnsen & Toeplitz †† have proposed mathematical methods of solution, the power of this analysis has never been tested beyond the simplest cases. In the table are given the values of  $d/n$ , calculated from  $n\lambda = 2d \sin \theta$  for sixteen of the stronger lines on the manganese pattern shown in No. 3, Pl. IV. There were faint indications of some other lines on some of the films, but they were omitted as probably spurious.

TABLE II.—Manganese Diffraction Pattern.

$d/n$ .	Intensity (estimated).	$d/n$ .	Intensity (estimated).
2.08 $\text{\AA.U.}$	8	1.23 $\text{\AA.U.}$	4
1.97	4	1.21	4
1.88	4	1.17	4
1.80	1	1.12	2
1.74	2	1.10	2
1.67	1	1.05	2
1.48	2	0.98	1
1.41	2	0.94	1

\* A. W. Hull, *Phys. Rev.* x. (6) p. 661 (1917).

† P. Scherrer, *Phys. Zeitschr.* xiv. p. 23 (1918).

‡ F. Kirchner, *Ann. d. Phys.* lxxix. (17) p. 59 (1922).

§ W. L. Bragg, *Phil. Mag.* xxviii. p. 335 (1914).

|| P. Groth, *Elemente der Phys. und Chem. Krystallographie*, 1921.

¶ A. W. Hull and W. P. Davey, *Phys. Rev.* xvii. (5) p. 549 (1921); *Journ. Opt. Soc. Amer.* v. (6) p. 479 (1921).

\*\* C. Runge, *Phys. Zeits.* xviii. p. 509 (1917).

†† A. Johnsen and O. Toeplitz, *Phys. Zeits.* xix. p. 47 (1918).



The value of the estimated intensity represents the relative intensity at least, and probably is a measure of the number of co-operating planes for each reflexion.

The photographs of the diffraction patterns of the alloys gave some interesting results, which are summarized in Table III.

TABLE III.—Crystal Structure of Heusler Alloys.

Alloy.	Condition.	$\mu$ max.	Remarks.	Crystal Structure.
III <i>a</i> .....	(1)	1.64	No magnetic field.	Face-centred cube, $d=3.70$ Å.U. (calculated from 5 lines).
III <i>a</i> .....	(1)	1.64	In a magnetic field of 3500 gauss.	Same as above.
III <i>a</i> .....	(2)	2.54	No magnetic field.	Same as above.
IV <i>a</i> ....	(1)	86.8	No magnetic field.	Face-centred cube, $d=3.70$ Å.U. (calculated from 5 lines); and, superimposed, a body-centred cube, $d=2.98$ Å.U. (calculated from 3 lines).
IV <i>a</i> .....	(1)	86.8	In a magnetic field of 3500 gauss.	Same as above.
IV <i>a</i> .....	(2)	14.6	No magnetic field.	Same as above.

Typical patterns of Alloys III *a* and IV *a* are shown in Nos. 4 & 5, Pl. IV.

It will be noted that in no case was there ever any trace on the films of the characteristic lines of any of the free crystalline elements—aluminium, manganese, and copper. This, of course, does not mean that they were completely absent in the alloy. It is unfortunate that the “sensitivity” of the X-ray method to detect the presence of small amounts of foreign crystals in a substance has never been worked out. Andrews\* mentioned that in the case of a mechanical mixture of zinc and copper powders it was quite easy to detect as low as 10 per cent. zinc, but the lowest limit is unknown. It would no doubt depend on the relative scattering powers of the two metals, but a value which might be proposed tentatively is 5 per cent. The writer hopes to be able to work out this feature of X-ray analysis in the near future.

\* Mary R. Andrews, Phys. Rev. xviii. p. 245 (1921).

## VI. DISCUSSION.

The fact that there was no evidence of the diffraction patterns of the individual metals—aluminium, manganese, and copper—was considered as indicating that these alloys in the conditions mentioned above were quite homogeneous, and that there had been no very great segregation of the constituents in the solidifying of the castings. A low percentage of the free metals would probably not be detectable. At the same time this would seem to dispose of the allotropic theory proposed first by Guillaume \*, and later by McTaggart and Robertson † and by Rhead ‡ in somewhat different forms, for this theory would admit the existence of free aluminium and copper along with a modified form of manganese in proportions which would easily be detected by the X-ray analysis.

The problem is then to find the structure of the Heusler alloy. It is unfortunate in this respect that the crystal structure of manganese is not known. Hull §, from a study of the structure of the ferromagnetic elements, has decided that the property of ferromagnetism does not depend on the arrangement of atoms, but on the distances between them. In the case of many of the elements and some binary alloys containing metals of similar atomic weights, this can be accurately ascertained; but in the case of binary alloys containing an element of low atomic weight and of ternary alloys, the present state of knowledge of X-ray diffraction makes it practically impossible to obtain a complete solution, even if the alloy does yield a perfectly definite diffraction pattern, as in the case of the Heusler alloys.

Ross's || explanation of the magnetic unit in these alloys accounted readily for the variation of magnetic properties, say with heat treatment, as a function of the relative concentrations of the binary alloys  $\text{Cu}_3\text{Al}$  and  $\text{Mn}_3\text{Al}$ . If this be true, there should be, in general at least, two crystal forms, giving diffraction patterns which in any one specimen should vary in relative intensity with change in magnetic permeability. The presence of two crystal lattices in the case of Alloy IVa might satisfy this theory, if the amounts of aluminium, manganese, and copper were just sufficient to make the binary alloys  $\text{Cu}_3\text{Al}$  and  $\text{Mn}_3\text{Al}$  in the proper proportions to give its magnetic properties in Condition (1);

\* *Loc. cit.*      † *Loc. cit.*      ‡ *Loc. cit.*

§ A. W. Hull, *Phys. Rev.* xiv. p. 540 (1919).

|| *Loc. cit.*

but as well as could be estimated, there was no relative change in intensity of the patterns when the magnetic permeability was reduced to about one-sixth of its previous value. An ionization method would have to be adopted for precision measurements. Further, Alloy III *a* showed only one crystal pattern, though its magnetic properties were of ferromagnetic magnitude, and by Ross's theory two lattices should be present. It is difficult to obtain correspondence between this theory and the results of the present experiments.

Heusler's\* explanation could be applied on the hypothesis that when the alloy was composed of certain proportions of the elements, as in Alloy III *a*, the complex compound  $\text{Al}_x\text{Cu}_a\text{Mn}_{(3x-a)}$  crystallized completely in a face-centred cubic lattice with which were associated the weaker ferromagnetic properties, as in nickel and cobalt; while for other proportions the crystallization could occur in two ways—a face-centred cubic lattice of the same dimensions as before, and also a body-centred lattice which would be attributed to a new complex compound. Then the stronger ferromagnetic properties would be associated with this new centred lattice, just as in the case of iron.

There has been an attempt† to explain the Heusler alloys as a series of solid solutions for which there has been considerable direct evidence. The work of Andrews‡ with zinc-copper alloys has shown that as much as 37 per cent. zinc may be dissolved in copper as a solid solution without altering the crystal habit of the copper. Above that percentage a centred cubic lattice appeared which was obtained in great purity with alloys of 50–60 per cent. zinc. It is possible that some such action takes place in the Heusler alloys. The manganese and aluminium may dissolve in the copper to form a solid solution, retaining the characteristic face-centred cubic lattice of copper but increasing its lattice constant from 3.60 Å.U. to 3.70 Å.U. due to the intrusion of the large Mn-Al complex group, which, like the zinc in copper, would not be detected by X-ray analysis. But for certain proportions of the constituents or for certain conditions of casting there may be produced a new centred cubic lattice, due to the Mn-Al complex, in sufficient quantity to give a diffraction pattern. The body-centred cubic lattice is certainly not due to any of the constituent metals as tested initially. It is natural to suppose it to be an alloy crystal.

\* *Loc. cit.*

† L. Guillet, *Soc. d'Encouragement, Rev. de met. Mem.* p. 87, 1906.

‡ *Loc. cit.*

The iron-nickel alloys investigated by Andrews\* and Kirchner† have shown crystalline habit analogous to that of the Heusler alloys. A particular nickel steel containing about 25 per cent. nickel can exist in two magnetic states. In the non-magnetic condition the X-ray pattern was found to be that of a face-centred cubic lattice, while in the magnetic state, produced by chilling in liquid air, there was present as well a body-centred cubic lattice. Again, the more ferromagnetic properties were accompanied by crystals of the centred cubic system. Hopkinson‡ found that these two states of nickel steel had different densities, viz. 8.15 and 7.98, for the non-magnetic and magnetic steels respectively. When these values were applied by Kirchner to determine the lattice constants for the crystals from the formulæ

$$d = \sqrt[3]{\frac{4 \cdot L}{N \cdot s}} \text{ for a face-centred cubic lattice}$$

and 
$$d = \sqrt[3]{\frac{2 \cdot L}{N \cdot s}} \text{ for a body-centred cubic lattice,}$$

where  $L$  is the "mean" atomic weight of the alloy obtained from the composition of the alloy,  $N$  is Avogadro's number, and  $s$  is the density, he obtained very good agreement with his experimental values. The same was found to hold in the case of the Heusler alloys. For Alloy III *a* the density 7.26 gave a value  $d = 3.60 \text{ \AA.U.}$  for the face-centred lattice, and from Alloy IV *a* of density 7.19 the value of the body-centred lattice constant  $d = 2.86 \text{ \AA.U.}$ , assuming that as an approximation the whole alloy was a body-centred cubic.

The attempt to produce a change in the diffraction pattern of the alloy by a magnetic field, due to the rotation or displacement of some magnetic particle, failed to give any positive result either in crystal lattice or in the intensity of the diffraction lines. This was to be expected from other experiments with X-rays. K. T. Compton and Trousdale§ found that the Laue pattern through a crystal of pyrrhotite or magnetite was unaffected by the action of a strong magnetic field on the crystal. A more sensitive method by ionization employed by A. H. Compton and Rognley|| failed to detect any change in the intensity of reflexion from a crystal face of pyrrhotite when in a magnetic field. The

\* *Loc. cit.*

† *Loc. cit.*

‡ Proc. Roy. Soc. xlvii. p. 138 (1889).

§ K. T. Compton and E. A. Trousdale, Phys. Rev. v. p. 315 (1915)

|| A. H. Compton and O. Rognley, Phys. Rev. xvi. p. 464 (1920).

absorption of gamma-rays by iron \* was the same, no matter what the magnetic state of the iron. The only positive results with regard to the effect of a magnetic field on X-ray phenomena have been obtained by Forman † and Becker ‡, who have obtained distinct variations in the absorption coefficients for X-rays of substances when placed in a magnetic field. The evidence to date points to the probable seat of magnetic phenomena in the behaviour and configuration of the outer or valence electrons. This, of course, is in agreement with the well-known changes in magnetic properties that take place as the result of chemical action, and those due to temperature variation which might be expected to have a direct influence on the loosely-bound valence electrons.

## VII. SUMMARY.

1. The crystal structures of aluminium, copper, and manganese have been studied by X-ray methods. The first two metals crystallized in a face-centred cubic system of lattice constant 4.05 Å.U. and 3.60 Å.U. respectively. The crystal structure of manganese has not been solved.

2. A study of two Heusler alloys of definite compositions and magnetic properties has shown that they occurred in two crystal forms—one a face-centred cubic crystal of constant 3.70 Å.U., and the other a combination of this same face-centred cubic crystal and a body-centred cubic crystal of lattice constant 2.98 Å.U.

3. These crystal habits of the Heusler alloys have been discussed in relation to the theories of the alloys, and evidence has been adduced indicating that they may be considered as solid solutions of manganese-aluminium alloy in copper. This is tentative, pending further experiments.

4. In no case was there any indication of the free constituent metals in the alloys, showing that they are homogeneous within the limit of "sensitivity" of the method of analysis.

5. In agreement with the crystallographic data of the ferromagnetic elements—iron, nickel, cobalt, and the alloy iron-nickel, which can assume a non-magnetic or magnetic condition—the more ferromagnetic Heusler alloy contained a body-centred cubic lattice, while the more weakly ferromagnetic one showed only the face-centred cubic lattice.

6. The variation of the magnetic properties of an alloy of

\* A. H. Compton, Phys. Rev. xvii. p. 38 (1921).

† A. H. Forman, Phys. Rev. iii. p. 306 (1914); vii. p. 119 (1916).

‡ J. A. Becker, Phys. Rev. xx. p. 134 (1922).

definite composition by suitable heat treatment produced no apparent change in the crystal form of the alloy.

7. The superposition of a magnetic field of 3500 gauss did not alter the crystal form of the alloys or make any noticeable change in the relative intensities of reflexion from the different crystal planes, indicating no change in orientation of the crystal unit.

8. Arguments have been presented tending to show that the ultimate magnetic unit is not the molecule or atom or any complex group of these, but that the magnetic effects are associated with the valence electrons.

In conclusion, the writer wishes to express his appreciation and thanks to Professor J. C. McLennan, who suggested the problem and has materially helped with the research, and also to the Honorary Advisory Council for Scientific and Industrial Research, Ottawa, Canada, who made this work possible by the award of a Fellowship.

University of Toronto,  
April 12th, 1923.

## XXIX. *Disintegration in Discharge Tubes.*

By H. P. WARAN, *M.A., Ph.D. (Cantab.), F.Inst.P.\**

[Plate V.]

### 1. *Historical.*

THE disintegration of discharge tubes may be divided broadly into two classes (*a*) the disintegration of the electrodes known as the sputtering, (*b*) the disintegration of the glass walls. Of these, the disintegration of the electrodes has been noted from very early times. Thus, as early as 1861, it had formed the subject matter of a paper by Gassiot † to the British Association. However, Sir William Crookes ‡ was the first to conduct a systematic investigation of the phenomenon using different metals for his electrodes. Recently Kohlschütter § and the research staff of the General Electric Co. || have investigated the phenomenon in great detail. On the other hand, very little is known about the

\* Communicated by Prof. A. W. Porter, D.Sc., F.R.S., F.Inst.P.

† Rep. Brit. Ass. ii. p. 38 (1861).

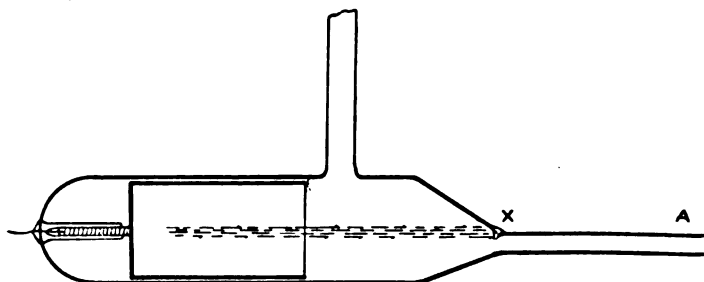
‡ Proc. Roy. Soc. i. p. 88 (1891).

§ *Jahrb. d. Rad. U. Elek.* ix. p. 355 (1912).

|| Phil. Mag. xlv. p. 98 (1923).

disintegration suffered by the glass walls, probably for the reason that its effects are not so very marked. But, as Dr. Coolidge \* has pointed out, in X-ray tubes that have failed from the cracks resulting from the chipping off of the glass in the neighbourhood of the cathode, such disintegration is prominently noticed. In special cases where the effects get accentuated by a focussing of the ions, the intense local heating melts the glass, and the pressure of the external atmosphere blows in a hole of the type shown at X in fig. 1.

Fig. 1.



In the present case a cylinder of aluminium formed the electrode, sending out a concentrated axial pencil of ions that hit the glass at X, the tube A not having been blown quite axial with the cylindrical electrode. In an earlier paper † on the subject I drew attention to the curious type of channels cut on the glass walls when a discharge is deflected on to it by a transverse magnetic field.

## 2. *Effect of the positive ions.*

As in the case of cathodic sputtering the agency responsible for the observed effect is mainly the ionic bombardment of the walls. Such a bombardment may bring about the disintegration, either mechanically or thermally, or by a combination of both actions. The apparent characteristics of the convergent set of markings first obtained led me to the suggestion that the markings are of the nature of tracks left by the motion of the particles along the glass walls. In that case it is the kinetic energy of the ion that is responsible for it. The lightest positive ion of hydrogen has a velocity about a tenth of that of an electron, a mass nearly 2000

\* Phys. Rev. xi. p. 409 (1913).

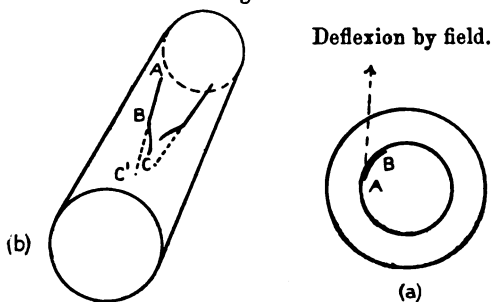
† Phil. Mag. xliii. p. 226 (1922).

times as great, and a kinetic energy about twenty times as great. Hence there was no doubt that the disintegration was produced mainly by the positive ions.

### 3. *A Mechanical Theory of Origin.*

The evidence in support of such a mechanical origin might be summarized briefly as follows. Firstly, the short light scratches on the glass could be imagined as arising from the sand-blast action of the swiftly moving positive ions moving towards the cathode, an equality in the energy of the particles accounting for the nearly equal length of the markings. Secondly, the peculiar shape and convergency of the tracks as shown in fig. 2, may be due to the deflecting

Fig. 2.



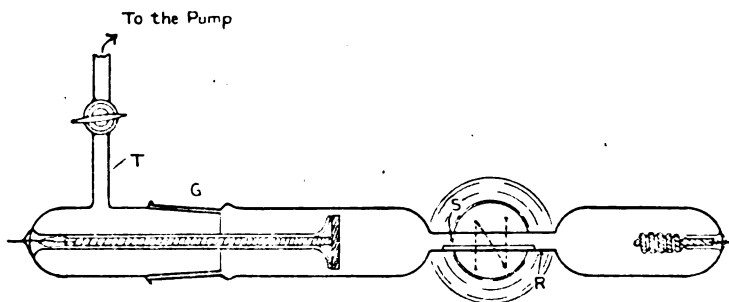
action of the transverse magnetic field. Let such a positive particle strike the cylindrical wall at A. So long as the particle has a sufficient forward velocity the magnetic field exerts a deflecting force at right angles to the axis of the tube. The cylindrical walls constraining such a motion, the particle can reach a higher level B only by travelling as shown in (a) along the cylindrical walls, and the track whose projection is AB is thus inclined to the axis of the tube. The bend BC towards the axis as shown at (b), may be due to the loss of velocity suffered by the particle after it has travelled the length AB, the particle of slower velocity being forced to a higher level C by motion along BC which is shorter than the straight path BC'.

Such an explanation, though fitting some of the facts observed, is obviously defective. For instance, in the absence of the magnetic field there is a uniform distribution of the positive particles across the cross-section of the discharge, and when they get deflected by the magnetic field



there is no reason why they are not striking the walls at azimuths other than those corresponding to the tracks observed. In fact, without any regularity, we ought to get a general corrosion of the glass. This point was tested with discharge tubes of the form shown in fig. 3.

Fig. 3.



A large ground joint at G permitted the easy introduction and withdrawal of test surfaces S of glass, mica, etc., introduced into the narrow region R, placed between the poles of a large electromagnet. Even after repeated trials with different gases at different pressures no markings of any kind could be seen on the test surfaces.

#### 4. *Energy Considerations.*

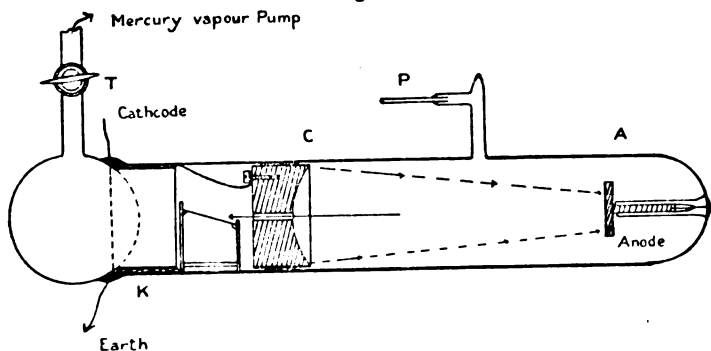
The observed tracks are in general about 2 millimetres in length, and about  $\frac{1}{2}$  millimetre in width, and their edges are quite ragged. Particles capable of effecting such a corrosion of the glass in virtue of their motion must have a very considerable energy associated with their motion. Goldsmith\* has shown that positive rays of hydrogen can be made to have velocities of the order of  $2 \times 10^8$  cm. a second, and that they pass readily through sheets of mica .005 mm. thick. The particles from radioactive sources are known to be capable of penetrating glass and mica surfaces to a depth of over .05 mm. and produce discoloration†. In a discharge tube the energy of the positive particle increases with the potential used for the discharge, and in a comparatively hard tube it would be interesting to examine the mechanical effect of positive rays on surfaces placed

\* Physical Rev. ii. p. 16 (1913).

† Rutherford, Phil. Mag. xix. p. 122 (1910).

against their path and look for any tracks of their motion on the surface. For this purpose a tube of the form shown in fig. 4 was used. A is a wide tube over an inch in diameter, and C is a massive aluminium cathode of the shape shown, having a central aperture for letting out the positive rays. Behind the cathode the test surfaces were arranged, at an angle of about  $20^\circ$  to the path of the rays, on a suitable wire frame rigidly fixed to the glass walls. A simple form of Gaede Langmuir mercury vapour pump was used to exhaust the tube, and being connected up as shown, it kept the space behind the cathode exhausted to a very low pressure, so that the loss of energy of the positive rays by molecular collision was kept low. To keep up the discharge a steady feed of

Fig. 4.

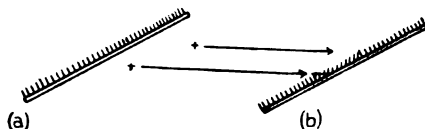


gas was introduced into the inter-electrode space through the platino-palladium tube P. Experimenting with glass and mica surfaces it was found that they got charged, and doubt was felt if the particles were not being deflected away by this charge. It was thought advisable to use conducting surfaces that could be earthed by a wire taken out through the wax joint at K. Though silvered surfaces are quite suitable for the purpose, it was thought better to use smoked surfaces of mica which are much more sensitive to any mechanical impact on them.

Experimenting with such an arrangement an intense beam of positive rays could be seen to strike the smoked surface causing an occasional scintillation, probably due to the disengaged smoke particles being raised to incandescence by the positive ray bombardment. Though the experiments were repeated at various gas pressures no traces of any tracks could be seen on the surface. However, within a few seconds of the bombardment there is a distinct change

in the reflecting power of the smoky surface over the area bombarded, indicating that the positive rays did produce a visible mechanical effect though of an order different from that expected. It was able to ruffle up the layer of carbon particles, which had a velvety structure of the type shown in fig. 5 (a), into a different orientation as indicated in fig. 5 (b) so that for the same angle of incidence the reflecting power of the two areas is different. By prolonging such positive ray bombardment for hours Stark and Wendt\* have obtained actual evidence for the corrosion of surfaces of glass, mica, etc. They observe, however, that though quartz is no harder than glass, very little effect is observed on quartz surfaces. This throws a doubt on the mechanical theory for the disintegration of glass surfaces. Further, positive ions having energies of this order are never met with under the conditions of our experiment where comparatively high gas

Fig. 5.



pressures and low potential discharges are used. Thus, though it is possible that the positive ion bombardment may be indirectly assisting the formation of such markings, the marks themselves can never be regarded as the tracks left by the motion of the positive particles along the walls.

### 5. *Connexion with the striations.*

An interesting property of these marks on the glass surface is their regularity and symmetry of distribution along the axis of the tube, a property displayed also by the striations, and it seemed possible that there might be some connexion between the two. In both cases of these phenomena the spacing has been found to vary with the gas pressure, and they are found to develop most readily in the case of discharge through carbon gases, which are noted for giving well marked cup-shaped striations. They are also found to lose their regularity when the positive column and the striations have ceased to exist. Thus, there is no doubt that the striations are intimately connected with such regularity as is observed in these marks.

\* *Ann. der Physik*, xxxviii. p. 921 (1912).

6. *A Thermal explanation for the marks.*

We have seen that the localized heating effect of ionic bombardment is very considerable. Stark and Wendt have observed that the surface gets quite red hot over the area bombarded. Quincke \* by his extensive researches on the thermal properties of glass has shown that in the neighbourhood of an electric discharge the localized heat might be sufficient to melt a superficial layer of glass, and on its subsequent solidification and cooling superficial fractures are developed. On such a thermal view of the phenomenon the observed difference between the behaviour of quartz and glass is only to be expected. The melting point of quartz is much higher than that of glass and, notwithstanding its higher thermal conductivity, even if a superficial layer of quartz does get fused it is not likely to develop cracks on cooling, since the coefficient of expansion of fused silica is very much lower than that of glass or quartz.

Such a thermal view of the phenomenon seems to be quite applicable to the type of disintegration under discussion even when the potential used to excite the tube is comparatively low. Though the positive particles have a higher energy at lower gas pressures the thermal effect might be greater at higher gas pressures when the current through the tube is a maximum, and the ionization by collision results in the production of a very large number of ions. It is also at this stage that the striations are most pronounced and the markings on the glass walls developed most readily. Further, R. W. Wood † has shown that corresponding to the striations there are zones of maximum heating in a discharge tube. Such zones of heating would be particularly pronounced when the striations are squeezed together into a small area by the deflecting field. An examination of the deflected discharge reveals the presence of the striations in it, and the observed markings on the sides of the tube are found to correspond to these striations. But straight line cracks at right angles to the axis of the tube as shown in Pl. V. (a) and (b), and irregular wavy cracks of the type shown in Pl. V. (c) and (d), are also frequently met with.

Even in the absence of a deflecting magnetic field cracks and markings of this nature are often found in discharge tubes, especially in the neighbourhood of the electrodes. Such defects develop rapidly, especially in the presence of

\* *Ann. der Physik*, xlviii. p. 113 (1915).

† *Wied. Ann.* xxxix. p. 238 (1896).

an initial deformation in the form of a scratch or opened air line in glass. Intense local heating is noticeable in such regions, and a number of minute cracks may also be seen on a microscopic examination of the surface. The existence of such incipient cracks in discharge tubes is proved by at least one well known observation. They have a marked tendency to crack off on the application of a blow-pipe flame, a tendency shared also by glasses that have long been in contact with radioactive material.

In conclusion I beg to express my indebtedness to the kind and sympathetic advice and guidance of Prof. A. W. Porter, D.Sc., F.R.S., in this work done at his laboratory.

### XXX. *The Velocity Constant of a Unimolecular Reaction.*

By JAMES RICE, M.A.\*

SEVERAL investigators have, during the past few years, devoted their attention to the elucidation of the problem of chemical reaction from its statistical side, basing their arguments either on purely statistical considerations or on a theory as to the nature of chemical reaction itself and the causes provoking it. At the same time free use has been made of some form of the Quantum hypothesis. A brief account of these researches will be found at the beginning of the paper by Mr. McKeown which follows this communication.

It would appear that the following formula for  $\kappa$ , the velocity constant of a unimolecular reaction, finds some experimental support, at least in the case of gaseous reactions; it is

$$\kappa = s \exp(-\epsilon/kT), \quad . . . . . (1)$$

where  $s$  and  $\epsilon$  are constants for a given compound dissociating into two components, and  $k$  and  $T$  have their usual significance. The quantity  $\epsilon$  is an amount of energy, usually called the "critical increment," and  $s$ , on simple dimensional grounds, must be a frequency. If one adopts the standpoint of the Quantum theory it is plausible to write

$$\epsilon = h\nu$$

and regard  $\nu$  as the frequency of some oscillatory process going on within the molecule, which leads to a rupture of the molecule when the amplitude of vibration has

\* Communicated by Prof. W. C. M. Lewis.

increased to such a point that the energy equals one quantum of energy for this frequency. On grounds which are largely empirical Dushman\* has suggested that  $s$  should also be equated to  $\nu$ , so that (1) should read

$$\kappa = \nu \exp(-h\nu/kT). \quad (2)$$

The object of this paper is to indicate that Dushman's equation (2), or one closely approximating to it, can be deduced very readily by a plausible "quantization" of an expression obtained some years ago by the writer and given by him in a discussion on Catalysis at the British Association meeting of 1915.

In order not to render the analysis unduly cumbersome we assume that for the purpose in view a molecule may be adequately represented by a simple mechanical model, in which two bodies are imagined as bound by a quasi-elastic force. We are only concerned with one coordinate which represents the distance apart of the two components and which is denoted by  $q$ . The introduction of other coordinates specifying all the remaining degrees of freedom of the molecule is unnecessary and would only serve to complicate the analysis with multiple integrals, which would disappear by cancellation in the final result. We assume that  $q$  may have any value from zero to infinity, and that the mutual potential energy,  $\phi(q)$ , of the two components increases with  $q$  until the separation  $q=c$  is reached; beyond the critical distance,  $c$ , the potential energy either decreases or remains constant. In the first case a supply of energy is required to enable the dissociated parts once more to enter into union; in the second case no energy is needed to ensure combination if the two constituents should encounter one another.

The energy of such a mechanism is given by

$$\epsilon = a\dot{q}^2 + \phi(q),$$

where  $a$  is in general a function of  $q$ .

The momentum is given by

$$p = 2a\dot{q}, \quad (3)$$

and so

$$\epsilon = p^2/4a + \phi(q).$$

Consider a system made up of such molecules, and let such an interaction take place between the molecules, or between these molecules and some other agent, such as gas molecules

\* J. Amer. Chem. Soc. xliii. p. 397 (1921).

or radiation, as is sufficient to bring about an exchange of energy between the various elements of the system. The exact nature of the means by which such exchange is produced is a matter surrounded with well-known difficulties, but the argument which follows is not immediately concerned with it and, being based on the existence of a state of equilibrium, is purely statistical. In such a state there will be present a definite number of undissociated molecules and also a definite number of the dissociated parts. The individuals in these two groups will change, but not their relative numbers. It is our business to calculate how many of the molecules will dissociate per second; this will, of course, be the number of pairs which recombine per second.

The number of undissociated molecules which are in the phase-extension  $q, p$  to  $q + dq, p + dp$  is

$$Ae^{-\mu\epsilon} dq dp,$$

where  $\mu = 1/kT$  and  $A$  is a constant\*.

We can represent the number of undissociated molecules by the double integral,

$$A \int_0^c \int_{-\infty}^{\infty} e^{-\mu\epsilon} dq dp. \quad . \quad . \quad . \quad . \quad (4)$$

The average value of any property,  $f$ , of these molecules is

$$\frac{\int_0^c \int_{-\infty}^{\infty} f e^{-\mu\epsilon} dq dp}{\int_0^c \int_{-\infty}^{\infty} e^{-\mu\epsilon} dq dp} \quad . \quad . \quad . \quad . \quad (5)$$

The rate at which the molecules dissociate is the rate at which they attain the condition in which  $q$  has increased numerically from a smaller value to the value  $c$ . The method of calculation is familiar. The number of molecules in the phase-extension  $c - \dot{q} \delta t, p$  to  $c, p + dp$  is obtained.

\* It is of course possible to question the validity of this expression under actual experimental conditions where a chemical reaction is going on and a state of statistical equilibrium between "reactants" and "resultants" has not been attained. However, in the case of those reactions which proceed at a rate sufficiently slow to enable measures of  $\kappa$  to be made, the critical condition for a molecule is so far removed from the average state that relatively few molecules are in this condition at one instant and their dissociation has but little influence on the statistical state of the undissociated molecules. In fact the use of the Maxwell distribution law here seems to be as justifiable as its use in the familiar treatment of viscosity and diffusion in the case of gases.

These will have passed the critical condition after an interval  $\delta t$  has elapsed \*. Since  $\dot{q} = p/2a$ , the number is

$$A \exp \{ -\mu [\phi(c) + p^2 / 4a] \} p \delta t dp / 2a. \quad (6)$$

Integrating from  $p=0$  to  $p=\infty$  and omitting  $\delta t$ , we obtain the rate of dissociation. It is

$$A e^{-\mu \phi(c)} \int_0^\infty e^{-\alpha p^2} p dp / 2a,$$

where  $\alpha = \mu/4a$ .

This is equal to

$$\begin{aligned} & A e^{-\mu \phi(c)} / 4\alpha a \\ & = kTA e^{-\mu \phi(c)}. \end{aligned} \quad (7)$$

The velocity constant,  $\kappa$ , is the quotient of (7) by (4),

$$\kappa = \frac{kT e^{-\mu \phi(c)}}{\int_0^c \int_{-\infty}^\infty e^{-\mu \epsilon} dq dp} \quad (8)$$

Since

$$\log \kappa = \log (kT) - \phi(c) / kT - \log \int_0^c \int_{-\infty}^\infty \exp (-\epsilon / kT) dq dp,$$

it follows that

$$\frac{d \log \kappa}{dT} = \frac{1}{T} + \frac{\phi(c)}{kT^2} - \frac{\int_0^c \int_{-\infty}^\infty \epsilon \exp (-\epsilon / kT) dq dp}{kT^2 \int_0^c \int_{-\infty}^\infty \exp (-\epsilon / kT) dq dp},$$

$$\text{by (5)} \quad = \frac{\phi(c) - \epsilon + kT}{kT^2}, \quad (9)$$

or practically

$$\frac{d \log \kappa}{dT} = \frac{\phi(c)}{kT^2}, \quad (9')$$

if the critical potential is large compared with the average energy of an undissociated molecule. This is now a well-known result and can easily be extended to a more general type of molecule, as Marcelin † first pointed out.

As stated previously the writer's object is to point out that if the expression (8) is modified in any one of several ways suggested by Quantum considerations, formulæ approximating to that of Dushman are obtained.

\* In order to avoid a digression we are overlooking an important point to which a reference will be made presently.

† *Ann. de Physique*, iii. p. 120 (1915).



The most obvious suggestion is to assign to the molecular model the properties of an harmonic oscillator ; *i. e.*, to regard  $a$  as a constant and put  $\phi(q)$  equal to  $bq^2$ , where  $b$  is another constant, so that the frequency of oscillation is given by

$$2\pi\nu = (b/a)^{\frac{1}{2}}.$$

The denominator in (8) then becomes

$$\int_0^c \int_{-\infty}^{\infty} \exp(-\alpha p^2 + \beta q^2) dq dp,$$

where  $\beta = \mu b$ .

$$\begin{aligned} \text{This expression} &= (\pi/\alpha)^{\frac{1}{2}} \int_0^c e^{-\beta q^2} dq \\ &= (\pi/\alpha\beta)^{\frac{1}{2}} \int_0^{c\sqrt{\beta}} e^{-x^2} dx. \end{aligned}$$

Since  $\beta c^2 = bc^2/kT$ , the integral approximates to  $\pi^{\frac{1}{2}}/2$  if the critical potential energy be large enough compared with  $kT$ ; *e. g.*, if  $bc^2 = 4kT$ , so that  $c\sqrt{\beta} = 2$ , the integral =  $\cdot 995 \pi^{\frac{1}{2}}$ . Even if  $bc^2$  is only equal to  $kT$  the integral is  $\cdot 843$  times  $\pi^{\frac{1}{2}}$ .

Hence the denominator in (8) is approximately equal to

$$\begin{aligned} &\cdot 5 \pi / (\alpha\beta)^{\frac{1}{2}} \\ &= \frac{\pi}{\mu (b/a)^{\frac{1}{2}}} \\ &= \frac{kT}{2\nu}. \end{aligned}$$

Hence

$$k = 2\nu e^{-\mu \phi(c)}.$$

If we assume that the critical potential energy is equal to  $h\nu$ , we have

$$k = 2\nu \exp(-h\nu/kT), \quad \dots \quad (10)$$

which is Dushman's expression multiplied by 2.

But Planck's treatment of the interaction of matter and radiation by means of an harmonic oscillator suggests that we might proceed with the quantization of (8) in a different manner. Thus considering a  $q, p$  diagram for the model we imagine it divided into annular elements by the curves of constant energy,

$$bq^2 + p^2/4a = \epsilon.$$

It is well known that the area of the elementary elliptical ring between the curves corresponding to  $\epsilon$  and  $\epsilon + d\epsilon$  is  $d\epsilon/\nu$ .

Let us postulate that all those molecules whose representative points lie within the ellipse of constant energy whose area is  $nh$ , are undissociated. This is equivalent to the assumption that dissociation takes place when the *whole* energy (attached to the coordinate  $q$ ) reaches the critical value of  $n$  quanta,  $nh$ , and not the potential energy alone. The number of molecules dissociating in time  $\delta t$  will then be represented by points in the  $q, p$  diagram lying sufficiently near to two of the quadrantal arcs of the  $nh$  ellipse.

It is necessary to point out before proceeding that we are involved in two assumptions here. The first is that the arrival of a representative point at the first and third quadrantal arcs of the critical ellipse is equivalent to a rupture of the molecule. To justify this we might say that at all events the molecule has become "active"; within a fraction of its period of oscillation the representative point, even without any further energy being acquired by the molecule, will have arrived at the position  $q=c$ , and the molecular configuration will be critical. The second assumption is concerned with a point which, as stated in the footnote on p. 315, was deferred for later consideration. In arriving at expression (6), we were clearly assuming that the molecule had sufficient energy to carry it up to the critical condition from the configuration  $q=c-\dot{q}\delta t$ . The calculation is purely kinematic and is of a type familiar in the kinetic theory of gases when treating viscosity, diffusion, etc. But in the gas applications the molecule is assumed to be on a *free* path with no retarding force acting on it, and it is legitimate to assume that it will maintain its velocity  $\dot{q}$  unchanged for the element of time  $\delta t$  and so will actually travel the distance  $\dot{q}\delta t$  as postulated in the calculation. But in the model assumed here, the separation of the molecular components is retarded by an attractive force and thus if the molecule is going to dissociate we must assume that the representative points of the molecules involved in expression (6) lie outside the constant energy curve

$$p^2/4a + \phi(q) = \phi(c).$$

Since the  $p$  coordinate of a point on this curve approaches the value zero as its  $q$  coordinate approaches  $c$ , we can satisfy this proviso if  $\delta t$  be taken sufficiently small. But in facing a similar difficulty with the idea that the "inactive" molecules are those represented by points within the critical energy curve we cannot dispose of it in so ready a manner. A point within this ellipse will not reach it, no matter how

near it is initially, *unless energy is supplied to the corresponding molecule*. Kinematically, the number of points reaching the ellipse in the time  $\delta t$  will be obtained by integrating

$$2A e^{-n\mu h\nu} \dot{q} \delta t dp$$

from  $p=0$  to  $p=p_m$ , where  $p_m$  is the maximum value possible for a point on the ellipse, so that  $p_m^2/4a = n h\nu$ . But, dynamically, we must postulate a supply of energy to the molecule during the interval  $\delta t$ , sufficient to maintain  $\dot{q}$  constant in order to justify this expression. A further treatment of this point seems desirable, but as this paper is concerned with the discovery of a statistical basis for Dushman's formula, the assumption will be made without further discussion at present. The writer hopes to return to this matter in a subsequent communication, as it appears to have some bearing on the well-known difficulty in the radiation theory of chemical reaction, pointed out some time ago in this journal by W. C. M. Lewis\*.

Proceeding with the argument as before, we obtain for the rate of dissociation of the molecules,

$$\begin{aligned} & 2A e^{-n\mu h\nu} \int_0^{p_m} p dp / 2a \\ &= A e^{-n\mu h\nu} p_m^2 / 2a \\ &= 2A e^{-n\mu h\nu} n h\nu. \end{aligned}$$

Under the circumstances (4) would apparently become

$$A \int_0^{n h\nu} e^{-\mu\epsilon} d(\epsilon/\nu),$$

which is equal to

$$\begin{aligned} & A \int_0^{n h\nu} e^{-\mu\epsilon} d\epsilon/\nu \\ &= A(1 - e^{-n\mu h\nu})/\mu\nu, \end{aligned}$$

so that  $\kappa$  should be given by

$$\begin{aligned} \kappa &= \frac{2n h\nu e^{-n\mu h\nu}}{(\mu\nu)^{-1}(1 - e^{-n\mu h\nu})} \\ &= 2n \frac{h\nu^2}{kT} \frac{1}{\exp(n h\nu/kT) - 1} \dots \dots (11) \end{aligned}$$

However, (11) is based on a partial application of the Quantum hypothesis, and requires reconsideration.

In that form of the theory which permits every point on

\* Phil. Mag. xxxix. p. 26 (1920).

the  $q, p$  diagram to represent an admissible physical state, it is nevertheless assumed that the Maxwellian law of distribution is modified by the postulate of finite regions of equal probability. For an harmonic oscillator these regions are the ellipse and the successive elliptic annuli, all of area  $h$ , which are bounded by the ellipses of constant energy which enclose area  $h, 2h, 3h$ , etc. Thus if there be  $N$  oscillators whose representative points lie in the first region, there are  $N e^{-\mu h\nu}$  with the points in the second,  $N e^{-2\mu h\nu}$  in the third, and so on. This will modify the preceding calculation as follows. The number of molecules dissociating in time  $\delta t$  will be obtained by integrating

$$2 \frac{N e^{-(n-1)\mu h\nu}}{h} \dot{q} \delta t dp,$$

since the density in phase of molecules whose points are in the  $n$ th finite region is

$$\frac{N e^{-(n-1)\mu h\nu}}{h}.$$

Hence the rate of dissociation is obtained as before to be

$$\begin{aligned} & \frac{N e^{-(n-1)\mu h\nu}}{2ah} p_m^2 \\ &= \frac{2N e^{-(n-1)\mu h\nu}}{h} n h\nu \\ &= 2n\nu N e^{-(n-1)\mu h\nu}. \quad \dots \quad (12) \end{aligned}$$

The number of undissociated molecules is

$$\begin{aligned} & N(1 + e^{-\mu h\nu} + e^{-2\mu h\nu} + \dots + e^{-(n-1)\mu h\nu}) \\ &= N \frac{1 - e^{-n\mu h\nu}}{1 - e^{-\mu h\nu}}. \quad \dots \quad (13) \end{aligned}$$

Dividing (13) by (12) we obtain

$$\kappa = 2n\nu \frac{e^{\mu h\nu} - 1}{e^{n\mu h\nu} - 1}. \quad \dots \quad (14)$$

If  $h\nu/kT$  be sufficiently large

$$\kappa = 2n\nu e^{-(n-1)\mu h\nu}, \quad \dots \quad (15)$$

and it is easy to deduce that

$$\frac{d \log \kappa}{dT} = \frac{(n-1) h\nu}{kT^2}. \quad \dots \quad (16)$$

So if we write  $\nu' = (n-1)\nu$ , we have

$$\kappa = \frac{2n}{n-1} \nu' \exp(-h\nu'/kT). \quad \dots \quad (17)$$

For purposes of numerical calculation (17) approximates to Dushman's formula, except for the factor 2, provided  $\nu'$  is calculated in the usual way from the equation for  $d \log \kappa / dT$  which becomes

$$\frac{d \log \kappa}{dT} = \frac{h\nu'}{kT^2}.$$

It should be observed that this result does not imply that an absorption band will be found at  $\nu'$ , but possibly only at a submultiple of it.

If  $\nu$  were too small (15) and (16) would not be so exact, and (14) would have to be used. Provided  $n$  were sufficiently great

$$\kappa = 2n\nu e^{-(n-1)\mu h\nu} (1 - e^{-\mu h\nu}). \quad . \quad . \quad (18)$$

This would produce a small change in (16), which would become

$$\frac{d \log \kappa}{dT} = \frac{h\nu}{kT^2} \left( n - 1 - \frac{1}{\exp(h\nu/kT) - 1} \right). \quad . \quad (19)$$

If  $n$  be unity, we obtain the peculiar result,

$$\kappa = 2\nu.$$

So that the assumption that the molecule ruptures for a critical energy of one quantum appears to lead to an enormous velocity-constant and one which is independent of temperature.

But, of course, Dushman's result is known not to be generally true. Its success seems to lie in gaseous reactions. This attempt to base it on statistical reasoning shows that it probably holds when the mechanism of the reaction is analogous to some such simple concept as the harmonic oscillator; but is altogether inadequate if the nature of the reaction is more complex.

These quantizations clearly rest on the implication that all physical states represented by a point on the  $q, p$  diagram are admissible. If we adopt the form of the Quantum theory, known as the "Stationary States hypothesis," which is employed in present-day atomic theories and in which only the points on the region boundaries represent admissible states, our method fails. One must start *ab initio* from postulates based on *a priori* probabilities of these states. Mr. McKeown shows in the following paper how the reasoning runs in that case.

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University of Liverpool.

XXXI. *The Velocity of a Unimolecular Reaction.*

By A. McKEOWN, M.Sc.\*

THE physical basis of unimolecular chemical processes has received considerable attention during the last few years. A semi-empirical method of investigation employed by Herzfeld (*Ann. der Physik*, lix. p. 613, 1919) depends on a combination of Stern's expression for the equilibrium constant of a unimolecular decomposition into atoms with the velocity of union of the atoms as given by the well-known collision expression. The resulting equation for the specific velocity of decomposition (velocity constant) is

$$k_1 = \frac{kT}{h} e^{-Q/kT} (1 - e^{-h\nu_1/kT}),$$

where  $k$ ,  $h$ ,  $T$  have their usual significance,  $Q$  is the heat of reaction per molecule, and  $\nu_1$  is the frequency of vibration of the atoms in the molecule. Dushman (*Journ. Amer. Chem. Soc.* xliii. p. 397, 1921) has recently compared the consequences of this formula with observation, and finds that the values of  $\nu_1$  calculated are many times greater than those deduced from specific heat data.

Such a method of approach as the above gives us no clue as to the mechanism of the unimolecular process itself; and, indeed, the expression for  $k_1$  may vary in form, depending on the particular degrees of freedom chosen as active in the molecule. Thus Trautz (*Zeitsch. für Physik*, ii. p. 113, 1920), working along similar lines, assumes no vibration of the atoms in the molecule, and his resulting expression is therefore

$$k_1 = \frac{kT}{h} \cdot e^{-Q/RT}.$$

For the radiation theory of chemical change, advanced by various writers during the last few years, the case of unimolecular processes has a special interest as distinct from reactions of higher order. In the case of a bimolecular reaction, the primary process of activation of the molecules by radiation is assumed to be very fast, so that the observed rate of reaction itself is governed only by the rate of collision of activated molecules. For the unimolecular case, however, collisions can play no part, and the velocity of dissociation should be governed by that of the process of activation—that is, the actual rate of interaction of matter and radiation should give an upper limiting value to the observed rate of chemical change.

\* Communicated by Prof. W. C. M. Lewis.

Working on this basis, W. C. M. Lewis (Phil. Mag. xxxix. p. 26, 1920) has attempted to obtain a value for  $k_1$  by equating the velocity of decomposition to the rate at which molecules obtain their critical increment  $h\nu$  by absorption from the surrounding radiation field. On the view of continuous absorption in accordance with Planck's second formulation of the quantum theory, the resulting expression for  $k_1$  is found to give values very much smaller than such velocity constants as have been experimentally observed. More recently, Lewis and McKeown (Journ. Amer. Chem. Soc. xliii. p. 1297, 1921) have attempted to account for this very great discrepancy, whilst retaining the concept of continuous absorption of radiation, by ascribing to the molecular field of action a concentrating effect, or what is the equivalent of a very high and practically constant refractive index of the order 200. Certain justifications of such an assumption have been offered, but whilst the expression obtained agrees well with observation it is felt that the picture realized is at best a very crude representation of the actual mode of interaction between radiation and matter.

Attempts have also been made by Lewis (*loc. cit.*) and Rideal (Phil. Mag. xl. p. 461, 1920) to apply the Einstein concept of discrete quanta of radiant energy to the case of a unimolecular chemical reaction. Activation of a molecule is considered to take place by collision with a quantum of the frequency corresponding to the activation process. Lewis ascribes to the quantum the diameter  $10^{-13}$  cm., whilst Rideal gives a value equal to the wave-length of the quantum itself. The velocity of the quantum is put equal to the velocity of light. Both writers, however, make use of an erroneous expression for collision frequency, so that their final results are invalid.

Dushman (*loc. cit.*) has suggested an empirical formula for the unimolecular velocity constant, viz.:

$$k_1 = \nu \cdot e^{-h\nu/kT},$$

and has shown this to be in agreement with existing experimental data (*cf.* Tolman, Journ. Amer. Chem. Soc. xliii. p. 269, 1921). The factor  $e^{-h\nu/kT}$  represents the fraction of activated molecules present at any instant, and the frequency factor  $\nu$ , identical with that in the exponential term, is taken to denote the frequency of some intra-molecular occurrence necessary for the decomposition of an activated molecule. Christiansen (*Zeitsch. für physik. Chem.* ciii. p. 91, 1922), in a discussion of the problem, has attempted to obtain a theoretical justification of Dushman's equation using

Einstein's particular conception of the mechanism of energy exchanges between molecules and radiation (*Physik. Zeitsch.* xviii. p. 121, 1917). Christiansen assumes that the process of activation corresponds to passage of a molecule by absorption of radiant energy from the normal state  $n$  to the activated state  $m$ , the difference of energy contents of these states being  $\epsilon_m - \epsilon_n = h\nu$ . If this difference be great, the number of molecules in the activated state under equilibrium conditions may be written :

$$N_m = N \cdot \frac{p_m}{p_n} \cdot e^{-h\nu/kT},$$

where  $N$  is the total number of molecules, and  $p_n, p_m$  denote the respective *a priori* probabilities of the states in question\*. When chemical change is possible, an activated molecule may either revert by emission to its normal state  $n$  or may pass by emission to another state  $n'$ , the latter passage being identified with the chemical decomposition. The states  $m$  and  $n'$  are also connected by the Bohr relation :

$$\epsilon_m - \epsilon_{n'} = h\nu'.$$

According to Einstein the probability of the change  $m \rightarrow n'$  may be written equal to  $(A_m^{n'} + B_m^{n'} u_{\nu'})$ , where the first term is the probability of spontaneous emission, and the second is the probability of the change occurring under the action of the thermal radiation field. Hence the rate of chemical change, which is controlled by this process, is

$$k_1 = \frac{p_m}{p_n} \cdot e^{-h\nu/kT} (A_m^{n'} + B_m^{n'} u_{\nu'}),$$

or using Einstein's expression for  $u_{\nu}$ ,

$$k_1 = \frac{p_m}{p_n} \cdot e^{-h\nu/kT} \cdot \frac{A_m^{n'}}{1 - e^{-h\nu'/kT}}.$$

Christiansen now assumes that the term  $A_m^{n'}$  which denotes the probability of the spontaneous change  $m \rightarrow n'$  may be written equal to  $\nu'$ , the frequency characteristic of the change. With this substitution his equation reduces to

$$k_1 = \frac{p_m}{p_n} \cdot e^{-h\nu/kT} \cdot \frac{\nu'}{1 - e^{-h\nu'/kT}}.$$

\* These *a priori* probabilities take account of the fact that each quantum state of definite energy content of a molecule may be realized in different ways, the  $p$ 's representing the number of possible modes of realization of each state.



For the case of small values of  $\frac{h\nu'}{kT}$  this formula approximates to

$$k_1 = \frac{p_m}{p_n} \cdot \frac{kT}{h} \cdot e^{-h\nu/kT},$$

comparable with the Herzfeld expression. For large values of  $\frac{h\nu'}{kT}$  Christiansen shows that the formula reduces to

$$k_1 = \frac{p_m}{p_n} \cdot \nu' \cdot e^{-h\nu/kT},$$

which bears a close formal resemblance to that of Dushman, the frequency  $\nu'$  being, however, essentially different from that occurring in the exponential.

It will be observed that the mathematical treatment of Christiansen is very analogous to the interpretation which Dushman gives to his equation. Both writers assume the possibility of the actual existence of activated molecules as apart from the dissociation products. Dushman then ascribes the decomposition of an activated molecule to coincidence of the state of activation with a particular static configuration of the molecule, this configuration occurring  $\nu$  times per second. Christiansen, however, associates the decomposition of an activated molecule with the occurrence of a more catastrophic phenomenon—the change  $m \rightarrow n'$  which takes place (for large values of  $\nu'$ ) approximately  $\nu'$  times per second. Christiansen's method of attack is the more revolutionary, and really involves a new and somewhat startling quantum electrodynamics, since he ascribes definite values to the A's and B's of Einstein's quantum dynamics, hitherto left undetermined by Einstein himself. This will be more clearly seen in the following treatment, which differs somewhat from that of Christiansen in that the separate existence of active molecules is not assumed, and therefore the rate of the dissociation is governed solely by the process of activation itself.

Consider a gas composed of similar molecules in equilibrium with temperature radiation (no chemical change assumed), each molecule capable of existing in a discrete series of states with energy contents  $\epsilon_1, \epsilon_2, \epsilon_3, \dots$ . In statistical equilibrium the numbers of molecules in the  $n$ th and  $m$ th states are given by

$$N_n = N \cdot A \cdot p_n \cdot e^{-\epsilon_n/kT}$$

and

$$N_m = N \cdot A \cdot p_m \cdot e^{-\epsilon_m/kT}$$

where  $p_m$  and  $p_n$  are the *a priori* probabilities of the states in question, and  $A$  is a factor independent of the state. Following Einstein, the probabilities of the transitions  $n \rightarrow m$  and  $m \rightarrow n$  in the time interval  $dt$  are :

$$d\pi = B_n^m u_\nu dt \quad \text{and} \quad d\pi = (A_m^n + B_m^n u_\nu) dt,$$

$n \rightarrow m$    $m \rightarrow n$

where  $u_\nu$  is the radiation density factor for the frequency  $\nu$  corresponding to the changes  $n \rightleftharpoons m$ . It follows that for statistical equilibrium

$$A_m^n p_m = u_\nu (B_n^m p_n \cdot e^{\overline{\epsilon_m - \epsilon_n}/kT} - B_m^n p_m).$$

If  $u_\nu$  increases without limit as  $T$  increases, then

$$B_n^m p_n = B_m^n p_m.$$

Writing  $A_m^n/B_m^n = K$ , Einstein obtains :

$$u_\nu = K / (e^{\overline{\epsilon_m - \epsilon_n}/kT} - 1).$$

Comparison with Planck's radiation formula shows that

$$\epsilon_m - \epsilon_n = h\nu$$

and

$$K = 8\pi h\nu^3/c^3.$$

Let us now assume, by analogy with Christiansen, that the probability per unit time of the spontaneous emission process  $m \rightarrow n$  is in general equal to  $\nu$ . It follows that  $B_m^n$  is equal to  $c^3/8\pi h\nu^2$ , and therefore also in general :

$$B_n^m = \frac{p_m}{p_n} \cdot B_m^n = \frac{p_m}{p_n} \cdot \frac{c^3}{8\pi h\nu^2}.$$

Hence the number of transformations  $n \rightarrow m$  per second in our system is given by

$$N_n \cdot \frac{p_m}{p_n} \cdot \frac{\nu}{e^{h\nu/kT} - 1}.$$

In a chemical system undergoing unimolecular decomposition, we may now consider that activation corresponds to the transition from the normal state  $n$  to the activated state  $m$ , and that the decomposition of an activated molecule is enormously more probable than the reversal  $m \rightarrow n$ , or, what seems more likely, that the activated molecule is identical with the decomposition products. The velocity of dissociation is then given directly by the rate of activation, and therefore by the above expression. For practically all

cases considered the  $\nu$  term is  $10^{14}$  to  $10^{15}$ , and therefore  $\frac{h\nu}{kT}$  is large compared with unity. Consequently  $N_n$  reduces to  $N$  and  $(e^{\frac{h\nu}{kT}} - 1)$  to  $e^{\frac{h\nu}{kT}}$ . Hence we obtain finally for the velocity constant of unimolecular decomposition :

$$k_1 = \frac{p_m}{p_n} \cdot \nu \cdot e^{-\frac{h\nu}{kT}}.$$

This equation differs from that of Dushman only in the factor  $\frac{p_m}{p_n}$  which may be greater or less than unity. For Bohr orbits in the generalized Sommerfeld sense,  $p_m$  would be greater than  $p_n$ , but in no case would  $\frac{p_m}{p_n}$  be a large numerical factor.

It will be obvious that the result obtained depends primarily on the assumption that  $A_m'' = \nu$ —that is, that the life of a stationary state  $m$  is equal, in the absence of radiation, to the period which characterizes the transitions  $n \rightleftharpoons m$ . The corresponding rate of absorption from a radiation field is very much greater than that given by classical electrodynamics. It may be noted that the expression for this rate does not contain in itself any of the properties of the absorbing system except the frequency  $\nu$ , and even this is only associated with the system for a particular transition.

The law of spontaneous emission should be that which governs radioactive transformations, unless these are dependent in some way on a very penetrating external radiation with  $\nu \simeq 10^{21}$ , as proposed by Perrin (*Ann. Phys.* xi. p. 5, 1919). This would make a radioactive change essentially a photochemical process as distinct from a thermal process considered above. (For a discussion of this distinction, cf. Lewis and McKeown, *loc. cit.*) It can, of course, be argued that since radioactive changes are never instantaneous but obey the unimolecular law some preliminary species of activation is necessary, whether this be dependent on the action of radiation in the Perrin sense, or merely on some fortuitous spatial orientation (independent of temperature) in the nucleus which decomposes.

#### *Summary.*

Applying Einstein's concept of the mutual action of radiation and matter, and making use of a postulate in

this connexion advanced by Christiansen, the following expression has been obtained for the velocity constant of a unimolecular chemical change :—

$$k_1 = \frac{\rho_m}{\rho_n} \cdot \nu \cdot e^{-h\nu/kT}.$$

This agrees formally with the empirical equation

$$k_1 = \nu \cdot e^{-h\nu/kT}$$

proposed by Dushman, and which has been shown by him to be in agreement with existing experimental data.

Department of Physical Chemistry,  
University of Liverpool.

XXXII. *Note on the Velocity of a Unimolecular Chemical Reaction.* By W. C. M. LEWIS\*.

ON the basis of the expression employed by Planck for the rate of absorption of radiant energy by an oscillator, the act of absorption being regarded as continuous, the author pointed out more than three years ago (*Phil. Mag.* [6] xxxix. p. 26, 1920) that an expression for the velocity constant of a unimolecular change could be obtained which involved, amongst other quantities, a refractive index term.

If the refractive index term is identified with that of a gaseous system as a whole, its value is practically unity. On this basis the expression for the velocity constant was found to lead to a value which was only one ten-millionth of that actually observed. Lewis and McKeown (*Journ. Amer. Chem. Soc.* xliii. p. 1288, 1921) attempted to account for this discrepancy by assuming a greatly increased value for the actual refractive index of the individual molecules, in semi-quantitative agreement with an earlier conclusion of Lamb regarding the dielectric constant of a molecule (*Trans. Camb. Phil. Soc.* xviii. p. 348, 1900).

It was felt, however, that to account for the discrepancy on the basis of the refractive index *within* the molecule was physically far from satisfactory. The experimental facts lead one to the conclusion—provided absorption of radiation is the physical cause of chemical change—that Planck's expression for the rate of absorption by an

\* Communicated by the Author.

oscillator gives a value which is far too low, unless we can assume *either* that the radiation density exhibits fluctuations and is locally condensed close to and around the individual molecules of every material substance, *or* that the oscillator is capable of drawing upon the radiation present in a volume which is great compared with the magnitude which might be attributed to the oscillator itself\*.

The latter possibility is attractive in view of a result obtained by the late Lord Rayleigh (Phil. Mag. xxxii. p. 188, 1916) on the rate of absorption by a *symmetrical* oscillator. It is doubtful whether it is legitimate to use this type of oscillator in the present case. Assuming that it is justifiable, we can make use of Lord Rayleigh's conclusion—namely, that such an oscillator in a given time will absorb the energy which passes through an area comparable with  $\lambda^2/\pi$ , where  $\lambda$  is the wave-length of the radiation concerned in the chemical change. This would mean that in one second the amount of radiation absorbed

is that which would be present in a volume  $\frac{\lambda^2}{\pi} \cdot \frac{c}{n}$ , where  $c$  is the velocity of light *in vacuo* and  $n$  the average refractive index of the system for this wave-length. The radiation density being  $u_\nu d\nu$ , the amount of energy absorbed by such an oscillator per second is given by

$$\frac{\lambda^2}{\pi} \cdot \frac{c}{n} \cdot u_\nu d\nu,$$

which becomes

$$8h\nu \cdot \frac{1}{e^{h\nu/kT} - 1} d\nu.$$

(It will be observed that the refractive index term has vanished.) For frequencies in the short infra-red, visible, and ultra-violet (which includes the chemically significant region), the expression becomes

$$8h\nu \cdot e^{-h\nu/kT} d\nu.$$

Dividing this by  $h\nu$ , we obtain the number of molecules each of which absorbs one quantum of the frequency  $\nu$  during one second, and consequently we obtain for the unimolecular velocity constant the expression

$$k_{\text{uni}} = 8e^{-h\nu/kT} d\nu, \quad \dots \quad (1)$$

where  $d\nu$  represents the width of the band or range of

\* In the long run these two possibilities may not be very different.

frequencies which the molecule is capable of absorbing round about frequency  $\nu$ .

The width of a band is usually defined as that spectral region over which the absorption coefficient falls to one-half of the maximum value which it possesses at the head or optical centre of the band (Ribaud, *Annales de Physique*, xii. p. 188, 1919). Ribaud (*Comptes Rend.* clxxi. p. 1134, 1920) considers that the width of a band (as distinct from that of a line) is defined solely by the position of the head of the band at which absorption occurs. Thus for band heads at 270  $\mu\mu$ , 500  $\mu\mu$ , and 3.3  $\mu$  Ribaud finds the corresponding widths to be 42  $\mu\mu$ , 77  $\mu\mu$ , and 720  $\mu\mu$  respectively. As a first approximation, therefore, we can write  $\lambda = 6d\lambda$  or  $d\nu = 0.17\nu$ . Equation (1) would then take the form

$$k_{\text{uni}} = 8 \times 0.17\nu \cdot e^{-h\nu/KT} \dots \dots \dots (2)$$

Owing to the approximate nature of the initial assumption—namely, that the oscillator absorbs the energy which passes through an area comparable with  $\lambda^2/\pi$ ,—it follows that no precision can be attributed to the numerical term ( $8 \times 0.17$ ). It would appear, however, that the expression (2) is capable of giving values comparable with those given by the empirical equation of Dushman, namely  $k = \nu \cdot e^{-h\nu/KT}$ , which, for the case of gaseous systems and for dissolved gases, has been found to accord fairly well with the experimental values, although it should be pointed out that very considerable discrepancies are found in the cases in which a *non-volatile* solute decomposes in solution in a unimolecular manner.

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### XXXIII. Note on the Chemical Constants of Diatomic Gases.

By J. R. PARTINGTON, D.Sc.\*

IN the Philosophical Magazine for November 1922 (vol. xlv. p. 988) I obtained an expression for the chemical constant of a diatomic gas which (equation 15 in the paper) is

$$\log_e \frac{m^{5.2} r^2 2^{7/2} \pi^{7.2} k^{7.2}}{h^5} \dots \dots \dots (1)$$

or  $C = 12.730 + 2.5 \log M + 2 \log r$

for the case of a molecule composed of two like atoms.

\* Communicated by the Author.

I now find that an expression reducing to the above had been found by the late Dr. Sackur by a slightly different method. In a paper in the *Annalen der Physik*, vol. xl. p. 98 (1913), he gives an expression which, when applied to the case considered, reduces to

$$C = 12.548 + 2.5 \log M + 2 \log r$$

and on p. 95 he obtains an expression (when the atoms are identical),

$$\log_e \frac{m^{5/2} r^2 2^{3/2} \pi^{7/2} k^{5/2}}{h^5},$$

which differs only by the addition of  $\log_e 2$  from (1), since the case investigated by Dr. Sackur was that mentioned on p. 993 of my paper, where it is stated that  $\log_e 2$  must be added. (Slightly different values for  $k$  and  $h$  were used by Dr. Sackur.)

I am still of the opinion that for a molecule composed of two identical atoms, the expression given by Dr. Sackur is in excess of the correct value by  $\log_e 2$ .

In my paper I also referred to the possibility of quantizing the angular momentum instead of the rotational energy; the latter would follow from the considerations advanced by Bjerrum\*: it is a very simple matter to modify the calculation, taking the expression  $\nu = nh / 4\pi^2 I$  instead of  $\nu = nh / 2\pi^2 I$ .

#### XXXIV. *On the Mechanism of the Electric Arc.*

*To the Editors of the Philosophical Magazine.*

DEAR SIRS,—

WITH reference to a recent contribution on the electric arc by Professor Duffield (June 1923) I am sorry to find that he and I are still in disagreement in the interpretation of the results he obtained. He criticises my use of deductions on the ionic distribution in the body of arc in the discussion of what takes place very near to the cathode. This criticism would be justifiable if we were concerned in his theory only with the repulsion of the cathode. But he explains the repulsion of the anode by postulating that electrons are projected from the cathode and communicate their momentum to the anode. Mr. Beer and I searched for them directly

\* *Ber. Deutsch. Phys. Ges.* xvi. p. 640 (1914).

and indirectly in the intervening space, the body of the arc which they would have to cross, and failed to find them there. I feel, therefore, that the failure of this test is a serious objection to his theory.

With regard to my suggested explanation of the repulsion of the poles I am afraid that I cannot have made my argument quite clear. Except close to the electrodes an ion travels with an average velocity determined by the field and the frictional drag of the ion on the gas. We are agreed that the resultant effect on the electrodes of this process is nil. But in the initial stage of its motion an ion starting from rest at the electrode surface must accelerate in order to acquire this average speed—in other words it is acquiring more momentum than it is imparting to the gas. I still maintain therefore that the electrode must feel the reaction whether the ion reaches its final average velocity rapidly or slowly. And whether an assumption such as I suggested, namely that the negative ions are charged atoms (which leads to a quantitative agreement with experiment) is justified or not, a reaction of some magnitude must be there.

Professor Duffield appears in one case to dislike my terminology. I do not quite see his reason for doing so. When ions moving from an electrode through a gas at atmospheric pressure exert a drag upon the gas they tend to set up behind them a region of lower pressure into which other gas or the electrode itself, if free, will move. I feel myself that the term 'suction' is a convenient and brief term for expressing this process.

I am,

Yours faithfully,

University of Bristol.  
June 11th, 1923.

A. M. TYNDALL.

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XXXV. *The Octet Theory of Induced Alternate Polarities: the Domains occupied by Octet-stable and Octet-unstable Centres.* By RONALD FRASER and J. E. HUMPHRIES, B.A., M.Sc., Chemistry Department, University of Aberdeen\*.

THE authors have recently (Chemical News, 1923, cxxvi. pp. 241, 257) applied the Lewis-Langmuir theory of covalence to the elucidation of the principles underlying numerous groups of facts and empirical rules in organic chemistry. The discussion rests primarily on an electronic

\* Communicated by Prof. A. Findlay, M.A., D.Sc.



interpretation of Lapworth's Principle of Induced Alternate Polarities, similar to that advanced by Kermack and Robinson (Jour. Chem. Soc. 1922, cxxi. p. 427). We differ from these authors, however, in postulating an electron transference as between stable and unstable octets as a necessary accompaniment of the manifestation of induced alternate polarity; that this is not their view was made clear by Professor Robinson at the Hull Meeting of the British Association, 1922. There appears to us to exist a certain amount of justification for our assumption: it is now widely recognized that there is no essential distinction between polar and non-polar compounds (G. N. Lewis, Jour. Am. Chem. Soc., 1916, xxxviii. p. 762; Briggs, Jour. Chem. Soc., 1921, cxix. p. 1879; Kermack and Robinson, *loc. cit.*; Stieglitz, Jour. Am. Chem. Soc., 1922, xlv. p. 1293); in an extreme case of the attainment of octet stability, such as that of the chlorine ion in the strongly polar compound NaCl, there is no doubt that electron transference has taken place; and it seems only in accordance with continuity to suppose that a chlorine atom in, say, monochlorobenzene has drawn an electron to itself from the carbon atom to which it is attached.

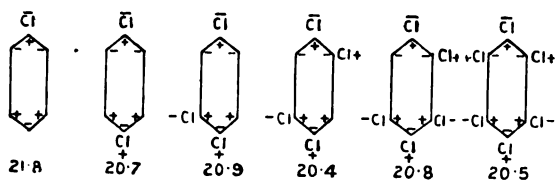
Further, in the extreme case of octet stability where the octet can exist free as an ion, its reactivity is exceedingly great; and we have found, in an examination of numbers of organic compounds in the light of the octet theory, that reactivity and octet stability run parallel. Perhaps it would be carrying the argument too far to assume ionization, even momentary, in such cases; but in any event it would appear that the more nearly a substituent approaches octet stability, the more it should spread from the nucleus. In view of the impossibility at present of determining the relative sizes of stable and unstable octets, we have been led by the above reasoning to seek a vindication of our opinion by considering the domains occupied by stable and unstable centres attached to the benzene nucleus.

Possible methods of attack include: (a) *Viscosity measurements*. An application to the present problem is immediately suggested of the methods employed by A. O. Rankine to determine the sizes of the protuberances formed by hydrogen atoms on molecules containing hydrogen (Rankine, Proc. Far. Soc., 1922, xvii. Part iii.). Unfortunately, the benzene derivatives we should wish to examine are liquids or crystalline solids, and an examination of these in the gaseous state, as would be demanded by Rankine's methods, presents considerable experimental difficulties: (b) *Critical data*. It has been pointed out by Chapman (Phil. Trans. Roy. Soc., 1916,

ccxvi. p. 279), that molecular sizes deduced from viscosity measurements and from the  $b_c$  of van der Waals' equation are in excellent agreement, for molecules containing up to three atoms. The bodies we should wish to examine contain six or more atoms, so that in such case too much faith could not be placed in the agreement noted by Chapman. There seems little doubt, however, that the foregoing are the best methods available; as has, indeed, been remarked by Wöhlisch (*Z. Elektrochem.*, 1921, xxvii. p. 295).

Owing to the time which must necessarily elapse before the results of extended inquiry along these lines may be available, we venture to think that the interest of the point at issue warrants our presenting here certain data which appear to lend support to our view, namely, that electron transference as between stable and unstable octets accompanies the manifestation of induced alternate polarity. We have made a re-examination of the work of Jungfleisch (*Compt. Rend.* 1867, lxiv. p. 911), and Le Bas (*Phil. Mag.* 1914, xxvii. p. 988), on the molecular volumes of various chlorobenzenes; we have taken merely the average volume of the chlorine atoms in each several compound, as we feel that the additive principle of Kopp can be pushed too far in investigations of this kind. Below are placed the ideographic representations of the compounds, with the state of octet stability and instability of the chlorine atoms indicated by — and + respectively. The figure beneath each compound is the average volume of the chlorine atoms, as computed

Fig. 1.



from the data of the authors mentioned. It will be seen that, in every case, the introduction of an octet-stable (—) chlorine causes an increase in the average volume of the chlorine atom, that of an octet unstable (+) chlorine a decrease, just as one would be led to expect on our view.

There is a further result of considerable interest; it might, in fact, be regarded as something in the nature of a crucial test. It will be observed that in all the compounds examined by Jungfleisch, certain of the chlorine octets are

stable, others unstable. Now, in the case of *m*-dichlorobenzene, we regard *both* chlorine atoms as in a state of octet stability; they are, therefore, reinforcing each other's tendency to spread from the nucleus; and hence, if our reasoning is correct, the average volume of the chlorine atoms in this compound should be greater than in any of the former cases where no such reinforcing effects existed. We have calculated the molecular volume of *m*-dichlorobenzene at the boiling-point (172°C.) from its density at 0°C. (1.307; Beilstein, vol. ii. p. 44) by means of the formula due to Le Bas (Proc. Chem. Soc., 1914, xxx. p. 86):

$$d_0/d_t = 1 + c \left( 1 - \frac{273}{B.P.} \right), \text{ where } c = 0.46.$$

The following figure gives the state of polarity of the constituent atoms of *m*-dichlorobenzene, and the average volume of the chlorine atoms, which may be taken to be correct to within 1 per cent. (Le Bas, *loc. cit.*). It should be compared with the first group.

Fig. 2.



21.5

The result is in accordance with prediction, the average volume of the chlorine atoms being about 3 per cent. greater than the largest value (20.9) obtaining in the polysubstituted members of the former group. (Monochlorobenzene appears to stand apart from the general run of the results.)\*

We consider the above data to give at least a pointer towards the correctness of our ideas, and, as such, to be of some interest; but it would be unwise to make any general statement at the present stage, until more extended results may be available for discussion.

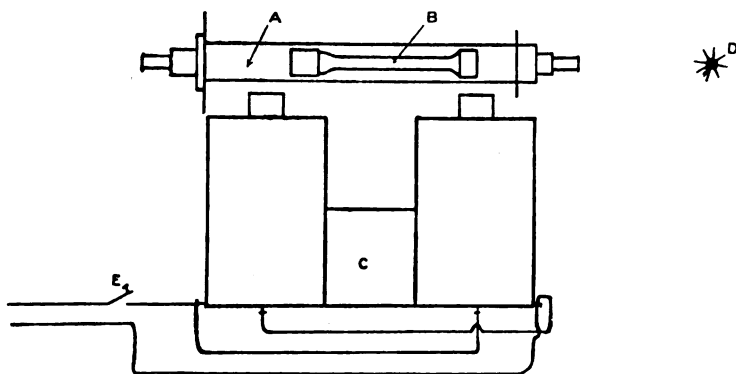
We are glad of this opportunity of expressing our gratitude to Professor Alex. Findlay for his interest and constant encouragement.

\* Fry ('The Electronic Conception of Valence and the Constitution of Benzene,' 1921, p. 177 seq.) has advanced a different interpretation of the results of Jungfleisch; but his theory leads to many inconsistencies, and it does not seem possible to predict, on the basis of his conceptions, the decided increase in the average volume of the chlorine atoms in *m*-dichlorobenzene.

XXXVI. *A New Phenomenon* \*. By MARSHALL HOLMES.

THE phenomenon to be described in this paper is thought to be new, and although it has a direct bearing on a larger question now being investigated, it is perhaps sufficiently interesting to warrant publication by itself.

The apparatus used was arranged in the manner shown:—



A is a polarimeter; B is the polarimeter cell containing a substance suitable for the investigation; C is an electro-magnet with the bobbins arranged across the bed; D is the source of light; and E is the switch. The nicols are arranged so that the polarimeter field appears uniform at first.

To obtain the phenomenon, the polarimeter cell is filled with a suitable liquid—glycerine was generally chosen—and placed in position in the polarimeter. The polarimeter field still appears uniform as glycerine is optically inactive. The current through the magnet is now switched on and the magnetic rotation produced causes part of the field to appear dark. If the adjustment of the polarimeter is left unaltered, and the current is now switched off again, attention being meanwhile steadily directed on the image, it will be seen that it first fades rapidly away and then just reappears with the light and dark parts reversed before the field finally becomes quite uniform, so that if the magnetic rotation has originally been *dextro* the reversed rotation is *levo*, or if it has been *levo* the change is to *dextro*. What happens with most substances is that the field becomes quite uniform immediately the current is switched off, and it remains uniform. With glycerine, however, such is not the case.

The phenomenon takes place and disappears very quickly,

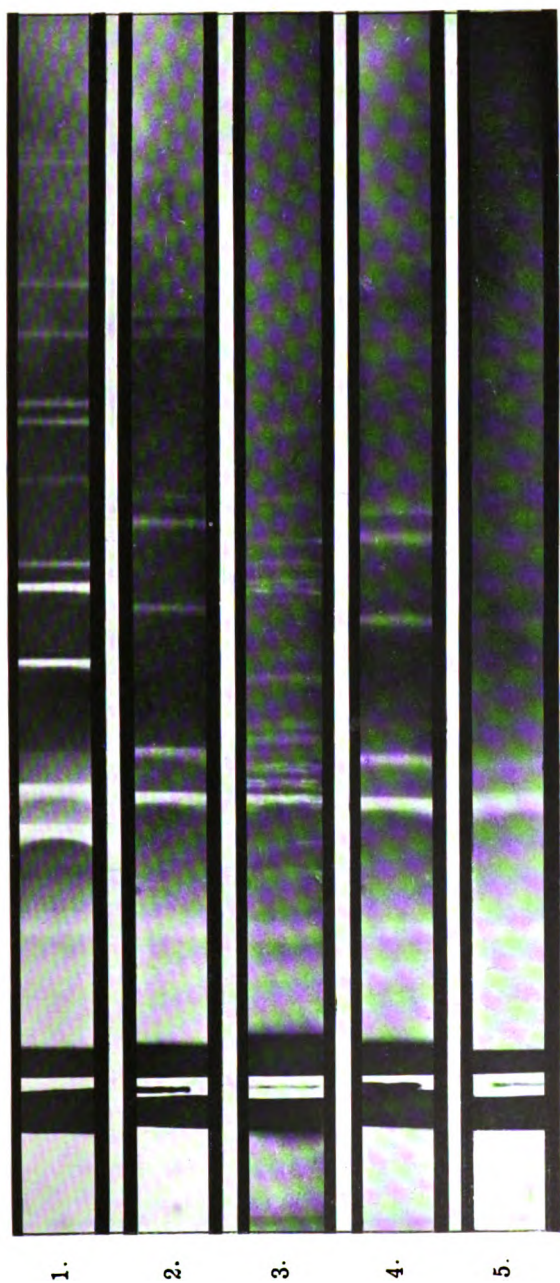
\* Communicated by the Author.

the average period elapsing from the time the current is interrupted till the field appears uniform being only a second or a second and a half long. The amount of reverse rotation is also very small ; it has never been found to be more than one degree of arc, and consequently it is rather difficult to observe. That there is a real rotation is shown, however, by the fact that it appears with only a very few liquids ; if the phenomenon were merely subjective it would be expected with all liquids. Those that showed it were glycerine, and solutions of citric acid in glycerine, and apparently also an aqueous solution of lead acetate slightly acidified with acetic acid. Liquids with a low or a very low viscosity did not exhibit the phenomenon ; glycerine, and certain solutions in glycerine with about the same viscosity, did exhibit it ; and still more viscous substances again failed to show any reversal, although one or two of the last appeared to show a slight lag in losing their magnetic rotation.

The simplest explanation seems to be furnished by the assumption that *magnetic molecules* exist in the liquid just as they are supposed to exist in a bar of iron, and that owing to the high viscosity each of these molecules has only a limited freedom of movement, that it has a position of metastable equilibrium ; consequently when the magnetic field is induced these molecules are placed in a state of strain, and when the stress is removed they swing past the positions of equilibrium and a rotation opposite to the magnetic rotation is shown. That the phenomenon does not occur when the viscosity is low may be due to either of two causes or to a combination of both ; possibly something does take place, but so quickly that the eye cannot follow the changes ; or more likely owing to the low viscosity of the liquid there is no position of equilibrium unless when the magnetic field is present. Another explanation is required for the absence of the reversal in liquids of a very high viscosity. In these cases a sufficient reason is probably furnished by the fact that the stresses due to the magnetic field are relatively small when compared with the stresses already existing in the liquid, so that when the magnetic field is removed only a comparatively insignificant change is made in the total of the forces present.

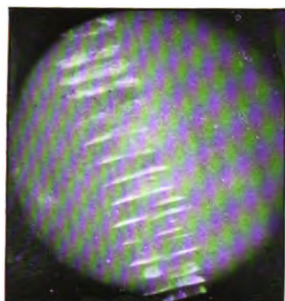
Before any hypothesis can be definitely accepted, however, much more work is yet to be done. All that is quite clear is that the phenomenon occurs.

The Sir Donald Currie Laboratories,  
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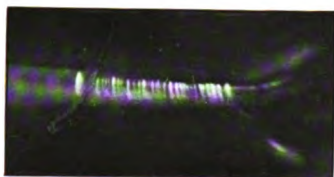


Powder Photographs of Al, Cu, Mn, Alloy III *a* and Alloy IV *a* in the order named.

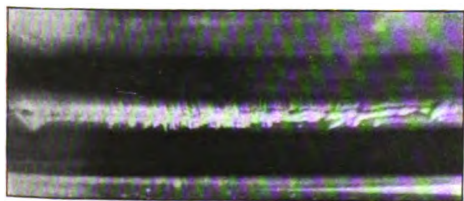




(a)



(b)



(c)



(d)





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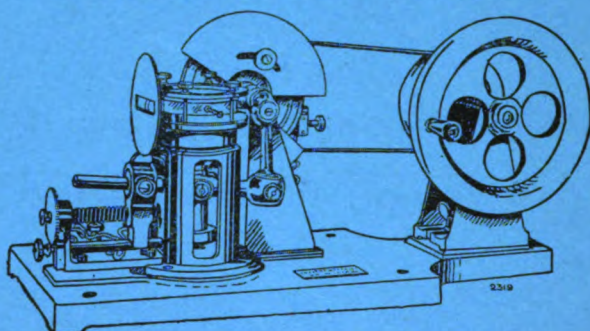
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XXXVII. *On the Energy in the Magnetic Circuit of a Magneto.*  
By N. W. McLACHLAN, D.Sc., F.Inst.P., M.I.E.E.\*

*Introduction.*

A PRELIMINARY treatment of this subject has been given in a former paper†. The cardinal points which emerged from the analysis were formulated on the basis of zero loss, and subject to the magnet always being worked at a point situated upon the hysteresis quadrant, i. e., a variation in reluctance caused the working-point to traverse the boundary line of the quadrant, and *not a subsidiary loop as it does in practice.*

It is the purpose of the present paper to treat the problem differently and more crucially, making assumptions which are in closer accord with practice—*e. g.*, no restriction has been placed on the shape of the armature; and to show that the optimum point for a magnet is not on the hysteresis loop at all, but on an auxiliary curve which is associated with the locus of the intersection of subsidiary loops and armature reluctance curves‡. The value of  $B$  corresponding to this optimum point is not necessarily equal to that on the main quadrant for which the product  $BH$  is a maximum. Owing to the nature of the formulæ for the energy obtainable from the magneto, there is a temptation to show that a physical concept of the electromagnetic energy associated with the

\* Communicated by the Author.

† 'Electrician,' July 30th and Aug. 6th, 1920.

‡ See fig. 7.

primary winding can be derived from the hysteresis quadrant by imagining the magnet to be an elastic medium which stores and restores the primary energy—i. e., a magnetic accumulator. It will be demonstrated that, so far as the present analysis goes, there is no substantial reason why the magnet and the primary should be correlated in such a fashion, and that any variations inherent in the magnet are due to changes in reluctance\* of the path followed by the magnetic flux which is common to the magnet and its external circuit. The energy concomitant with such variations is associated, through the medium of the armature, with the external source causing rotation.

In Part I. it was shown that the energy of magnetized iron was a subject for experimental investigation before any definite formula giving the value could be established. Pending the production of such data, it will be assumed that the unknown factor  $Q$  to which reference was made is numerically equal to  $\frac{1}{\mu}$ , where  $\mu$  is the permeability of the pole-shoe and armature iron.

#### *Elementary Analytical Treatment.*

##### HYPOTHESES A.

- (1) There is no loss incurred as the armature rotates, whether the winding is open or closed on itself.
- (2) The flux through the magnet and its external circuit is constant from make to break.
- (3) The magnetic leakage is zero, and the flux density in the magnet limbs is uniform.
- (4) The working-point for the magnet is situated on the main hysteresis loop.
- (5) On open circuit the reluctance does not vary with the position of the armature.
- (6) The armature is never run continuously on short-circuit—i. e., the demagnetizing influences are merely those which accompany normal running where no short-circuit device is employed to suppress sparking at the plug.

#### *Derivation of Energy Equations.*

In fig. 4 is shown diagrammatically the hysteresis quadrant of the magnet steel obtained by some approved method when the metal forms a closed magnetic circuit. OA is the reluctance curve of the armature for varying flux densities—i. e., it shows the relation between the

\* This may be caused by armature reaction, eddy currents, or variation in the configuration of the magnetic circuit.

flux density and the value of  $H$  necessary to impel the flux through the armature, air-gaps, and pole-pieces. The flux density in the magnet is that corresponding to  $X$ , and the total flux through the circuit is the product of this ordinate and the cross-sectional area of the magnet. We will now derive an expression for the electromagnetic energy stored in the primary circuit when the armature rotates on closed circuit from the position of fig. 1 to that of fig. 2 or 3.

From the familiar equation to the magnetic circuit, we have at make (refer to fig. 1):

$$H_1 l_m = N_1 \rho_1, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where

$H_1$  = external m.m.f. due to demagnetizing force on magnet caused by armature reluctance,

$l_m$  = mean length of magnet which may be taken along neutral axis from centres of pole-pieces,

$N_1$  = total flux through magnet,

$\rho_1$  = reluctance of path external to magnet.

For figs. 2 and 3, at break we can write

$$H_1 l_m + 4\pi ni = N_1 \rho_2, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where

$ni$  = armature ampere turns,

$\rho_2$  = reluctance of external path traversed by flux.

From hypotheses (2) and (3) the magnet and armature fluxes are constant, and therefore  $H_1$  is the abscissa of the point  $X$  in fig. 4 or 8. The path external to the magnet which is traversed by the flux has a greater reluctance in the position of fig. 2 or 3 than in that of fig. 1, and the m.m.f. to overcome the additional reluctance is supplied by the armature in virtue of the current in its winding; in fact, the armature current due to induction during rotation from make to break is concomitant with the alteration in reluctance. As a first approximation, we will assume that the self-inductance in figs. 2 and 3 position is defined symbolically by

$$Li = Nn, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where

$L$  = self-inductance of armature in position of figs. 2 and 3,

$i$  = armature current (abs. units),

$n$  = „ turns,

$N$  = total flux cut during rotation from make to break.



Transforming (2), we get

$$ni = (N_1\rho_2 - H_1 l_m)/4\pi.$$

Fig. 1.

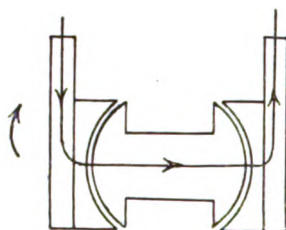


Diagram showing configuration with armature at  $-90^\circ$  to mid-position.

Fig. 2.

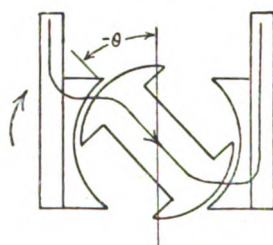


Diagram showing configuration when break occurs *before* mid-position.

Fig. 3.

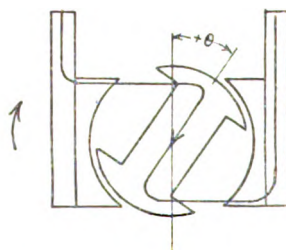
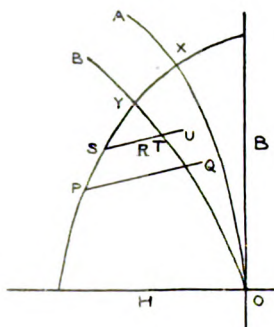


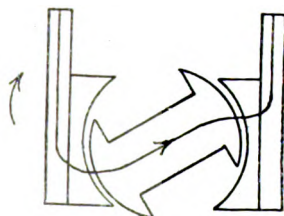
Diagram showing configuration when break occurs *after* mid-position.

Fig. 4.



Hysteresis loop, armature reluctance curves and subsidiary lines.

Fig. 5.



Configuration when make occurs before  $-90^\circ$  position.

Substituting from (1),

$$\begin{aligned} ni &= (N_1\rho_2 - N_1\rho_1)/4\pi \\ &= \frac{N_1}{4\pi}(\rho_2 - \rho_1). \end{aligned} \quad (4)$$

Now energy  $W = \frac{1}{2}Li^2 = Li \cdot i/2,$

and substituting for  $Li$  from (3)

$$W = \frac{Nni}{2}. \quad (5)$$

Substituting the value of  $ni$  from (4) in (5), we obtain

$$W = \frac{NN_1}{8\pi}(\rho_2 - \rho_1). \quad (6)$$



If we write  $\rho_2 = p\rho_1$ , where  $p = \text{a constant}$ , equation (6) becomes

$$W = \frac{NN_1}{8\pi} \rho_1 (p-1),$$

which on substitution from (1) gives

$$W = \frac{NH_1}{8\pi} l_m \cdot (p-1). \quad . \quad . \quad . \quad (7)$$

Now  $N$ , the flux cut by the armature during rotation from make to break, depends upon the angular movement  $\theta$ , and may be written

$$N = N_1 \phi(\theta),$$

where  $\phi(\theta)$  is a function of  $\theta$ .

Hence, substituting in (7) for  $N$ , we get

$$W = \frac{N_1 H_1}{8\pi} l_m \phi(\theta) (p-1),$$

and since  $N_1 = B_1 A$ ,

$$W = \frac{B_1 H_1}{8\pi} \phi(\theta) \cdot (p-1) \times \text{volume of magnet};$$

or

$$\text{Energy per unit volume of magnet} = \frac{B_1 H_1}{8\pi} \cdot Z, \quad . \quad (8)$$

where  $Z = \phi(\theta)(p-1)$  and  $B_1 H_1$  is a point on the hysteresis quadrant.

This expression is similar to (16) obtained in Part I. ('Electrician,' July 30th, 1920).

### *More detailed Analytical Treatment.*

In order to proceed with the analytical treatment, we must modify some and discard others of the old hypotheses. The variation in reluctance of the circuit external to the magnet has been disregarded hitherto, when the armature revolves with the primary open-circuited. In general, the reluctance in the position of fig. 1 is a minimum, and increases until at  $90^\circ$  thereto it reaches a maximum value. The variation is of the order of 25 per cent.

Suppose a magneto to be assembled and the magnet to be energized *in situ*, the armature occupying the position illustrated in fig. 1. The working-point on the hysteresis

quadrant will be X in fig. 8. If the armature is rotated on open circuit to a position  $90^\circ$  ahead of fig. 1, X (in fig. 8) will travel down the quadrant to P, which is the intersection of the quadrant and the armature reluctance curve for the new position. Between X and P we have a series of reluctance curves for the different angular positions of the armature. If rotation is continued until the conjugate position of fig. 1 ( $180^\circ$  ahead) is attained, the magnet operates along a subsidiary loop PQ which is represented by a straight line, this being a conveniently close approximation\*. Further and continued rotation on open circuit results in a cyclic movement round the subsidiary loop. Concomitant with the variation in reluctance of the external circuit there is a variation of the energy stored in the system. From Q to P work is done in rotating the armature, and energy is stored in the system external to the magnet. It can be shown that at P the energy in the external system per unit volume of magnet, in the absence of armature current, may be written  $\frac{B_1 H_1}{8\pi}$  and at Q,  $\frac{B_2 H_2}{8\pi}$ †. Hence the work done during rotation from the position of fig. 1 through  $90^\circ$  is  $\frac{(B_1 H_1 - B_2 H_2)}{8\pi}$ .

In the latter position (mid-position) the armature is in a state of unstable equilibrium; for in the absence of external constraint—*e. g.* friction, eddy current, and hysteresis loss—if it is moved from its initial position either clockwise or anticlockwise, it will fly back to the configuration of fig. 1 or its conjugate. When, however, it reaches either of these positions, it has attained a certain velocity and travels on through  $90^\circ$  in virtue of its momentum. If any energy is added externally when the motion commences, the armature will pass through the latter position and continue to rotate *ad infinitum*. In practice, since there are considerable losses due to hysteresis and eddies in the core and surrounding metal masses, the armature executes a damped oscillation about one of the positions indicated in fig. 1, and finally comes to rest there. The number of oscillations is a rough measure of the total damping on open circuit. The damping is of course due to the combined effect of electrical and mechanical losses. This flyback or unstable phenomenon is well known, and the principle is used in certain forms of

\* Watson, Journal I. E. E. vol. lix. p. 449 (1921).

† Evershed, Journal I. E. E. vol. lviii. p. 780 (1920).

electromagnetic relay. During the oscillatory motion, the energy relation can be expressed in the following form :

$$\begin{aligned}
 &\text{Work done during rotation from position of fig. 1 (1) to} \\
 &\quad \text{position (2) } 90^\circ \text{ ahead minus loss incurred} \\
 &\quad = \text{Initial potential energy of position (2),} \\
 &\quad = \text{Potential + Kinetic energies in any intermediate} \\
 &\quad \quad \text{position} \\
 &\quad + \text{Total loss from time oscillation started.}
 \end{aligned}$$

We will now deal with the problem when the armature circuit is closed at make and opened at break. Starting from Y (fig. 4) with a machine whose magnet has just been magnetized with the armature in fig. 1 position, let rotation occur until the configuration of fig. 3 is attained. The armature current increases from zero, and in so doing it constrains the flux to pass through the core. The point Y remains fixed until mid-position, *i. e.*  $90^\circ$  ahead, is reached. Beyond this point the field due to the armature current opposes the magnet, and the point Y moves down the quadrant until the point S\* is gained, where we will assume that the contact-breaker opens and the spark occurs. The primary current is suddenly reduced to zero and then reversed, due to the oscillation which follows break. As the primary current oscillates after break, the point S moves up and down a subsidiary line SU. The final state of the magnet when the current is zero is at the point R, this being the intersection of the armature reluctance curve for the particular armature position, and the subsidiary line. In this discussion we have tacitly assumed that there is no lag between the current changes in the armature and the flux changes in the magneto. This is not so in practice owing to eddy currents. The current having decayed to zero, and the armature rotation having been continued, the reluctance decreases until the conjugate position of fig. 1 is reached, when the working-point for the magnet is T in fig. 4. The primary closes once more and the cycle of operations is repeated, the magnet operating along the line SU. The point S is attained due to the largest demagnetizing force exerted by the armature, and in a magneto which was never short-circuited, except during the normal "make" period, the location of this point would depend on the position of the timing lever at full retard. If, however, the magnet was subjected to high-speed short-

\* It is assumed that S is further down the quadrant than the intersection of the reluctance curve for mid-position.

circuit conditions, the point S would be further down the quadrant and the working-line would be PQ.

With the aid of this explanatory matter we can now apply the foregoing analytical methods, with the essential modifications.

#### HYPOTHESES B.

- (1) From  $\theta = -90^\circ$  to  $\theta = 0^\circ$  (mid-position) the magnet flux and the external or demagnetizing m.m.f. exerted on the magnet are constant; from  $\theta = 0^\circ$  to the point of break the magnet flux decreases, and the external m.m.f. increases by an amount dependent on the angular movement beyond mid-position.
- (2) There is no loss in either the magnet or the armature.
- (3) There is no magnetic leakage, and the flux density in the magnet limbs is uniform.
- (4) The flux changes in the whole magnetic circuit are simultaneous.

At make we have (fig. 1)

$$H_1 l_m = N_1 \rho_1, \quad . . . . . (9)$$

and for break *before or at* mid-position

$$H_1 l_m + 4\pi ni = N_1 \rho_2. \quad . . . . . (10)$$

For a point of break beyond mid-position

$$H_2 l_m + 4\pi ni = N_2 \rho_2 + \psi(\theta) \cdot 4\pi ni, \quad . . . (11)$$

where  $\psi(\theta)$  is a function of  $\theta$ , and the other symbols have the same meaning as previously. The term  $\psi(\theta) 4\pi ni$  represents the demagnetizing effect due to the armature current beyond mid-position.

By hypothesis,

$$(H_2 - H_1) l_m = \psi(\theta) \cdot 4\pi ni. \quad . . . . . (12)$$

Thus, combining (11) and (12), we obtain

$$H_1 l_m + 4\pi ni = N_2 \rho_2. \quad . . . . . (13)$$

From (9) and (10) we get

$$ni = \frac{N_1}{4\pi} \cdot (\rho_2 - \rho_1),$$

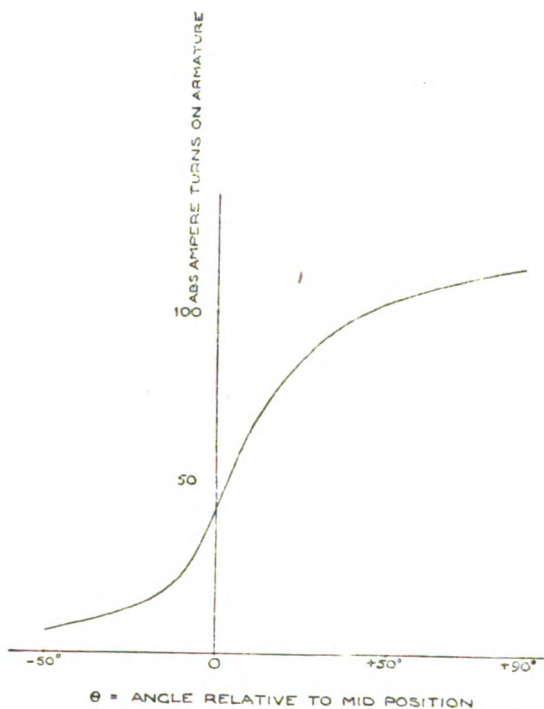
which is identical with (4). Since  $Li = Nn$  (see (3)), we find with the same reasoning as that used in obtaining (8), that for a point of break prior to mid-position,

$$\text{Total energy } W = \frac{B_1 H_1}{8\pi} \cdot Z \times \text{volume}, \quad . . . (14)$$

where Z depends on the angular movement of the armature

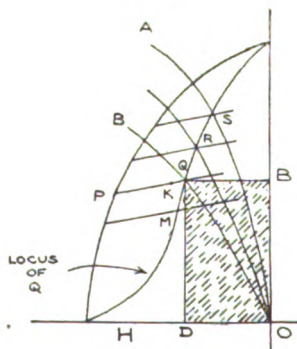
from make to break, and  $B_1$ ,  $H_1$  are the coordinates of the point Q in figs. 7 and 8.

Fig. 6.



Curve showing relation between armature ampere-turns and angular position of armature, the total flux being 26,800 lines.

Fig. 7.



Showing locus of intersection of armature reluctance curves and subsidiary lines.

For a point of break *beyond mid-position* :—

From (9) and (13),

$$ni = (N_2\rho_2 - N_1\rho_1)/4\pi.$$

Putting  $N_2 = N_1$ , as it is approximately in practice, and  $\rho_2 = p\rho_1$ , we get

$$ni = \frac{N\rho_1}{4\pi} (p-1). \quad (15)$$

From (5),  $W = \frac{Nni}{2}$ , where  $N = N_1\phi(\theta)$  as in (8).

Substituting the value of  $ni$  from (15) in the last equation,

$$W = \frac{N_1^2}{8\pi} \cdot \rho_1 \cdot (p-1)\phi(\theta). \quad (16)$$

Since  $H_1 l_m = N_1 \rho_1$  and  $N_1 = B_1 A$ , (16) becomes

$$\begin{aligned} W &= \frac{B_1 H_1}{8\pi} \cdot (p-1) \cdot \phi(\theta) \cdot \text{volume of magnet} \\ &= \frac{B_1 H_1}{8\pi} Z \text{ per unit vol. of magnet,} \end{aligned} \quad (17)$$

where  $Z = (p-1)\phi(\theta)$ , and depends on the position at break relative to that at make—i. e., on the angular movement of the armature, and  $B_1, H_1$  are the coordinates of the point Q in fig. 8. If the magnet has been subjected to short-circuit conditions, Q will be further down the curve AXO of fig. 8.

In equations (8), (14), and (17) the factor Z appears. Its value cannot be computed mathematically to any degree of accuracy, but fortunately the components embodied therein can be ascertained experimentally for any given type of magneto. Thus if Z is found empirically, the validity of the analysis can be tested by measuring the total spark-energy, allowance being made for loss during transformation, and comparing the result with that computed from (14) or (17) according to the point of break. If make occurs at a point other than that depicted in fig. 1, say fig. 2 or fig. 5, it is sufficiently accurate to take the values of  $B_1$  and  $H_1$  at the position in question. The armature reluctance curve will be different in each case.

The available energy is given by the expression  $\frac{Nni}{2}$ , and this is equivalent to

$$\frac{4\pi ni}{l_m} \cdot \frac{B_1 A l_m}{8\pi} \cdot \phi(\theta) = \left[ \frac{4\pi}{2 \cdot 4\pi} \cdot \frac{l_m}{l_m} \cdot N_1 \phi(\theta) \right].$$

Thus the energy per unit volume of the magnet is  $\frac{4\pi ni}{l_m} \cdot \frac{B_1}{8\pi} \phi(\theta)$ . This expression could of course have been obtained much earlier in the treatment, but it does not contain the factor  $H_1$ , and would by itself be of no assistance in the final issue when the optimum magnet is derived. Equating the latter expression for  $W$  per unit volume of magnet to that found in (17), we obtain

$$\frac{4\pi ni}{l_m} \cdot \frac{B_1 \phi(\theta)}{8\pi} = \frac{B_1 H_1}{8\pi} \cdot (p-1) \phi(\theta)$$

or  $(p-1) = \frac{4\pi ni}{H_1 l_m} \cdot \dots \dots \dots (18)$

Moreover, in order to determine  $(p-1)$  experimentally, the armature is fixed in definite positions, and the current required to maintain the working flux is found for each position. This yields  $ni$ , the armature ampere-turns for various angular positions. An actual curve is illustrated in fig. 6. The only point which remains indefinite is that during actual working a variation in flux occurs, due to demagnetization of the magnet when the armature is beyond mid-position; but this is not sufficiently serious to be taken into account for the angular movements which occur in practice. If the curve showing flux for various positions with the armature on open circuit is found (see fig. 9), also the data of fig. 8, the value of  $Z$  can be computed from the expression

$$Z = (p-1) \phi(\theta) = \frac{4\pi ni}{H_1 l_m} \cdot \frac{N}{N_1} \cdot \dots \dots \dots (19)$$

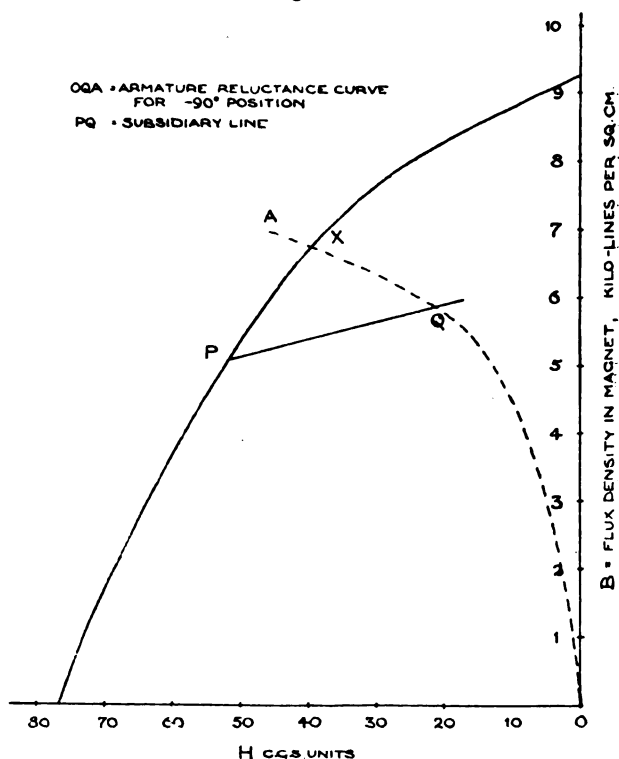
#### *Computation of the Factor Z.*

In fig. 6 \* is shown what may conveniently be termed an armature reluctance curve, in which the ampere-turns to maintain the working flux in various angular positions are plotted against the angular movement of the armature from mid-position. Fig. 8 shows the hysteresis quadrant, armature

\* The author is indebted to Mr. E. A. Watson for figs. 6 and 8, and data connected therewith.

reluctance curve for  $-90^\circ$ , and a subsidiary line; whilst fig. 9 gives the *assumed* relationship between flux through the armature on open circuit and the angle from mid-position.

Fig. 8.



Hysteresis loop, armature reluctance curve and subsidiary lines for actual machines.

By aid of these diagrams the results given in the Table were obtained.  $Z$  was computed, using equation (19).

The mean length of the magnet on neutral axis . . . . . = 25 cm.,

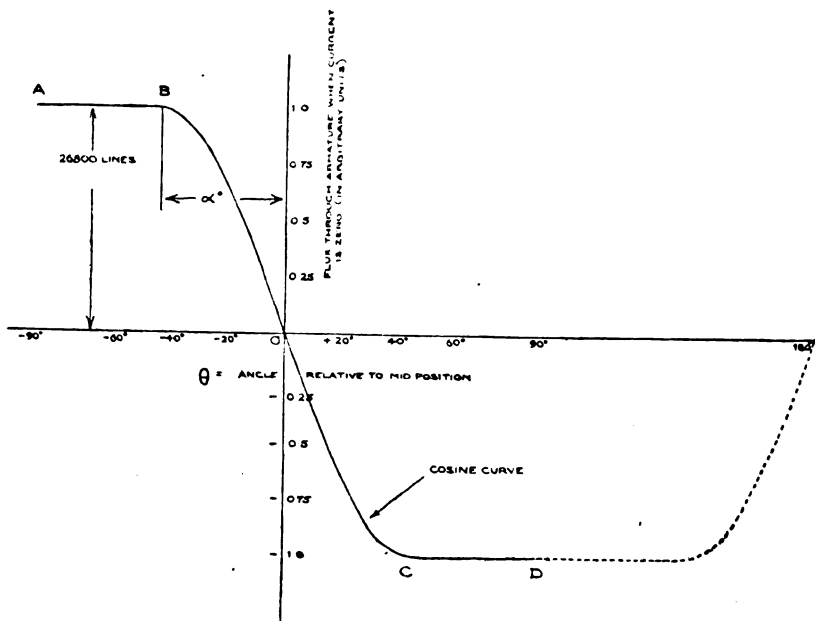
and the

Cross-sectional area of the magnet . . = 4.62 sq. cm.



In fig. 10 is plotted the available energy for various armature positions, this of course being in the present instance directly proportional to  $Z$ . Since energy  $= \frac{1}{2} Li^2 = kZ$ , where  $k = \frac{B_1 H_1}{8\pi}$  vol., the armature current, assuming the inductance to be invariable, is proportional to the square root of the energy, and to that of  $Z$ . This is illustrated by the curve

Fig. 9.



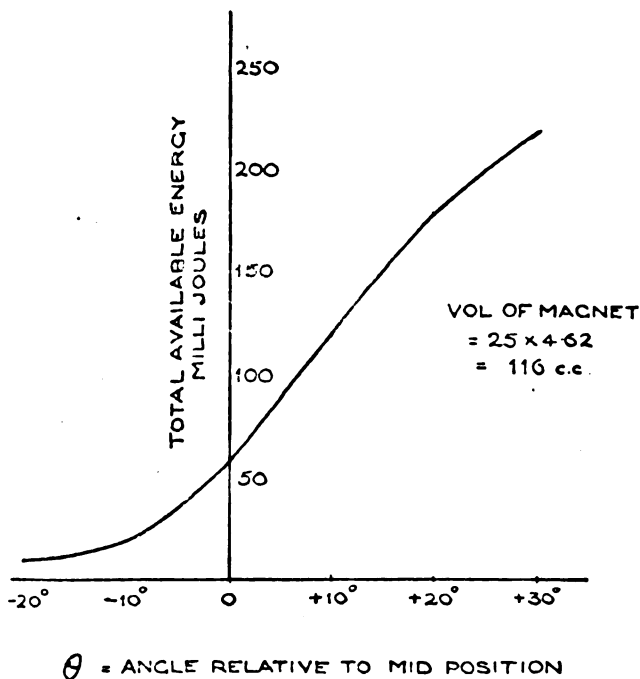
Curve showing relation between flux through armature and angle relative to mid-position.

of fig. 11. In all cases the change of curvature is rather abrupt, like the characteristic of a rectifier, owing to the shape of the flux curve of fig. 9, which we assumed for simplicity to be a cosine curve with straight horizontal pieces extrapolated. In practice the top of the curve is not quite straight, and due to its being rounded off the energy and current curves do not change curvature so abruptly as those shown here.

*Determination of Conditions for Maximum Energy with a Magnet of Fixed Dimensions.*

Having already obtained an expression for the available energy associated with the primary winding in terms of commensurable coefficients of the magnetic circuit, the next step is to ascertain the condition under which the energy with a magnet of fixed dimensions has its maximum

Fig. 10.



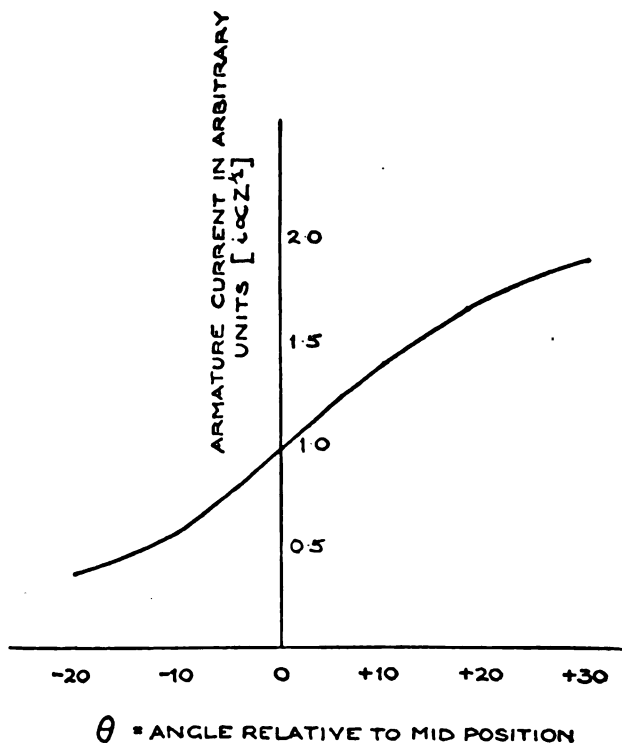
Curve showing total available energy from magneto with a magnet 4.62 sq. cm. in cross-section and 25 cm. mean length, for various points of break, make occurring at  $-90^\circ$ , there being zero loss during rotation.

value. The first case to be considered will be one in which the armature diameter and length are fixed.

After the armature has been run on short-circuit at high speed, we get the graphs shown on fig. 7, where PQ is the working or subsidiary line. When the armature is at  $-90^\circ$  to mid-position the magnet is worked at Q, and

when operating under short-circuit conditions \* the magnet functions from P up and down the subsidiary line. The energy obtainable when the machine is functioning normally (*i. e.* there is no short-circuiting) is equal to

Fig. 11.



Curve showing relation between armature current at break, in arbitrary units, for various angular positions, make occurring at  $-90^\circ$ , there being zero loss during rotation.

$\frac{B_1 H_1 Z}{8\pi}$  ergs per c.c. of magnet, where  $B_1$  and  $H_1$  are the coordinates of the point Q. For a certain value of the air-gap the graphs PQ and BQO are obtained. If the air-gap be varied (either increased or decreased) the graphs will also alter, and for a series of air-gaps there will be a corresponding series of graphs, each yielding a different

\* In this case the primary is closed for one or more revolutions of the armature. Thus there is no spark at the plug.

TABLE.

The circuit is made at  $\theta = -90^\circ$ , and broken at the values in column 1.

$\theta$ = Angular position of armature at break relative to mid-position. (Degrees).	$H_i$ on subsidiary line. (c.g.s. units.)	$B_i$ on subsidiary line. (Lines per sq. cm.)	Turns $\times$ absolute amperes.	Total flux change between make & break / $N = N_i = B_i$	Flux at make $p = l.$	Z.	W. Available energy for magnet of 116 c.c. volume. (Millijoules.)
-20	23	5800	15	0.36	0.33	0.15	9.2
-10	"	"	22	0.66	0.48	0.32	20
0	"	"	43	1.0	0.94	0.94	60
+10	"	"	66	1.34	1.44 *	1.98 *	120
+20	"	"	81	1.64	1.77 *	2.9 *	180
+30	"	"	91	1.87	1.9 *	3.55 *	217

\* The variation in  $B_i$  is neglected.

working line for the magnet. The energy obtainable in every instance is dependent on the product of the co-ordinates at Q, R, etc. It is necessary, of course, that the magnet should be re-magnetized before securing each individual working line. The locus of the point Q is a curve of the form drawn in fig. 8. This curve is determined empirically for any particular type of magneto.

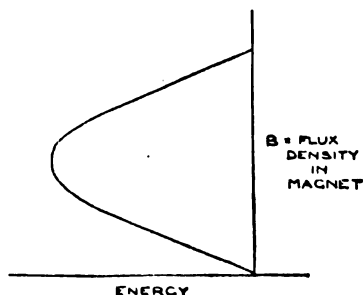
We may write

$$\begin{aligned} Z &= (p-1)\phi(\theta) \\ &\text{as before (see (19))} \\ &= \left(\frac{\rho_2}{\rho_1}-1\right)\frac{N}{N_1}. \end{aligned}$$

There is a possibility that  $\frac{\rho_2}{\rho_1}$  and  $\frac{N}{N_1}$  will vary with the air-gap, and therefore the best policy is to ascertain the value of  $Z$  for the different air-gaps as shown in the section immediately preceding.

Having found the various factors in the expression  $\frac{B_1 H_1 Z}{8\pi}$ , it now becomes possible to draw a curve showing the relationship between energy and  $B_1$  for any given point of break. The value of  $Z$  depends evidently on the latter, and there is a family of energy curves for various points of break. In every instance the curve will have a maximum

Fig. 12.



Curve showing energy relationship for given magnet and varying flux density in magnet.

energy value (see fig. 12), and the air-gap corresponding to this will be the optimum. Clearly there will be an optimum value of  $B_1$ , and this may vary for different points of break, although the variation might be inappreciable from a practical view-point. It would be a lucky coincidence if  $BH$  were a maximum on the main loop for the same value of  $B$  as

that on the energy curve at, say, full retard, this timing position being associated with the slowest speeds. From a practical standpoint it is desirable that such a coincidence should occur, and more particularly if all the optimum  $B$ 's for various points of break were identical. In general, the shape of the energy curve is similar, excepting for small values of  $B$ , to that exhibited in fig. 12.

*Determination of Optimum Armature Diameter when Magnet, Air-Gap, and Armature Length are fixed.*

It ought to be evident from the preceding section that the optimum  $B_1$  and corresponding energy obtainable from the machine is, with a given magnet, chiefly a question of armature reluctance. Having fixed the gap and the magnet, the procedure is similar to that above, excepting that the armature diameter is varied. In all probability, for any definite point of break or ignition, the values of  $B$  for optimum gap or armature diameter will not be very different.

*Determination of Optimum Magnet when Armature, Magnetic Section, and Air Gap are fixed: Consideration of a further problem.*

Having found the optimum value of  $B_1$  for the particular brand of magnet steel, as set forth above, the length of the magnet is arranged so that the flux density is identical with  $B_1$  where the working subsidiary line intersects the armature reluctance curve. This gives the maximum energy from the magneto per unit volume of magnet steel for the cross-section in question; nevertheless, the amount of energy might be inadequate. In such a case the machine would have to be re-dimensioned, or a larger magnet used—in which latter circumstances the optimum conditions would not hold. The solution of the problem indicated here is approximate, since there may be a variation in  $Z$ . A more accurate answer could be obtained by varying the length of the magnet until the required value is obtained.

There is another case which apparently arises, viz.: to find the optimum magnet \* so that the magnet can supply a definite amount of energy. From the analysis already given, it will be clear that the energy obtainable from the machine (in the primary winding) does not depend solely on the magnet, and that the energy per unit volume of magnet

\* The magnet of minimum volume for which the energy from the machine has a prescribed value.

may vary according to the relative proportion of magnet, air-gap, and armature. At present no definite solution can be offered, but with a large accumulation of practical data it will doubtless be possible to frame a good working rule applicable to a certain class of magneto.

*The Pseudo-relationship between the Energy in the Primary and Energy Storage in the Magnet.*

In attempting to correlate the variation in energy in the primary circuit with a similar variation in the magnet, the latter is imagined to be an accumulator which is virtually charged and discharged as the primary circuit is opened and closed. As a popular method of explaining the action and function of the magnet this might find favour, but we will endeavour to show that there does not exist any evidence to warrant the scientific accuracy of such a statement. Referring to fig. 7, suppose the working-line is PQ; then the magnet, under normal operation, functions from Q at make to K at break, the latter point not being far from the former. Assuming for simplicity that the points are coincident, the energy per unit volume of magnet is proportional to the shaded area, *provided Z be constant for all points of break*. But the latter condition is not satisfied, as the results in the Table clearly testify. Since there is little movement from Q to K\*, the shaded area remains approximately constant during operation (make to break), and therefore, apart from Foucault currents in the metal masses, the magnet enjoys a comparatively undisturbed career until of course the spark occurs or the armature is short-circuited†. With these subsequent actions we are, however, not concerned meanwhile. Moreover, this constancy of condition precludes any accumulation or decumulation of energy within the magnet structure to a degree which can be approximately equal to that liberated from the primary at break. Hence we are compelled to conclude that the electromagnetic energy associated with the primary circuit is derived entirely and continuously from the source causing rotation of the armature, and that the magnet is merely an agent or accessory which enables this energy phenomenon to occur, just as in a Wimshurst machine the frictional effect of the brushes plays a somewhat similar part. So far as motion along the line PQ is concerned, it is easy to apprehend that, apart from eddy-current effects in the magnet, the magnet is perfectly

\* Assuming make at  $-90^\circ$  and break at mid-position or  $0^\circ$ .

† See previous footnote on p. 352.

elastic. There is, however, prior to break, no potential energy variation in the magnet of a magnitude approaching that of the primary energy at break.

Owing to the mechanical reaction between magnet and armature, there is a potential energy relationship; for were the armature (carrying current) fixed, and the magnet free to move, motion would ensue, thus converting potential energy into kinetic energy. This, however, is an issue of a purely mechanical nature, resulting from electrical action at a distance.

It is of interest to speculate on the energy in the primary if make occurs at  $-90^\circ$  and break occurs at  $+90^\circ$ , this being of course quite beyond the limits which practice demands. In the latter position the demagnetizing force on the magnet is considerably reduced due to leakage, and we may assume that the external m.m.f. is balanced by the armature current, and that the latter is also sufficient to maintain the final flux \*. Thus the current is approximately of such a value that its m.m.f. is twice the external m.m.f. of the magnet. Hence, for this terminal position,  $4\pi ni = 2H_2 l_m$ . Substituting in the equation

$$W = \frac{B_2 H_2}{8\pi} \cdot Z = \frac{4\pi ni}{l_m} \cdot \frac{B_2 N}{8\pi N_1},$$

$$\left[ \text{since from (19) } H_2 Z = \frac{4\pi ni}{l_m} \cdot \frac{N}{N_1} \right]^\dagger$$

we get, since  $N = 2N_1$ ,

$$W = \frac{2H_2 l_m}{8\pi l_m} \cdot \frac{2N_1}{N_1} \cdot B_2 = \frac{B_2 H_2}{2\pi}$$

per unit volume of magnet,

where  $B_2 H_2$  is on the hysteresis quadrant.

In this case we are tempted to correlate the area  $B_2 H_2$  with the primary energy, but it is well to remember that the initial conditions were at the point  $B_1 H_1$ , and if any relationship were formulated, it would have to include the area  $B_1 H_1$ . This, however, would hardly meet the circumstances, unless the point  $B_1 H_1$  were situated upon the axis of B. Such a condition would necessitate zero reluctance for the  $-90^\circ$  position at make, and this does not occur in practice. When the expression  $B_1 H_1$  is used in conjunction with a permanent magnet as shown herein, the value obtained represents the energy in the system *external to the magnet*.

\* This is slightly less than the original flux at  $-90^\circ$ , owing to the demagnetizing effect on the magnet.

† It is assumed as at top of p. 347, that  $N_2 = N_1$ .



*The Influence of Armature Resistance.*

This phase of the subject is all-important in practice, since the effect of resistance is greatest on full retard at slow speeds, especially when starting in cold weather. If the resistance is zero, as we have assumed hitherto, the available energy is independent of the speed of rotation, provided there are no other losses. It may be well to state, therefore, that the term "effective resistance" includes the effect of all losses from make to break, and that the ohmic resistance of the armature means the d.c. resistance of the winding. For the sake of illustration, assume the current rise from make to break is sinusoidal:

then  $i = \frac{E}{(R^2 + \omega^2 L^2)^{\frac{1}{2}}}$ . If  $R$ , the effective resistance, is small compared with  $\omega L$ , then  $i = \frac{E}{\omega L}$ , this being the value for a resistanceless coil of inductance  $L$ . This condition is satisfied approximately at high speeds, where the current is nearly constant over a wide range of speed.  $E$ , the induced e.m.f., varies directly as the speed; so does  $\omega$ : hence, if  $L$  is assumed constant,  $i$  is independent of speed. With the magneto it is well known that the voltage and current waves depart considerably from sinusoidal formation. Thus, in order to deal with the problem mathematically, we must either resolve the voltage wave into its harmonic components, using Fourier's theorem, or adopt a simpler procedure. The assumed relationship between the flux through the armature and the angle of rotation from  $-90^\circ$  is shown in fig. 9. The configuration from  $-180^\circ$  to  $+180^\circ$  approaches that of a rectangular flux wave. Assume  $AB$  in fig. 9 to be parallel with the  $\theta$  axis, and  $BC$  to be a portion of a cosine curve whose period is smaller than that of the flux alternations. From  $A$  to  $B$  we have the relationship  $N = N_1$ , and from  $B$  to  $C$   $N = N_1 \cos \theta = N_1 \cos \omega t$ , where  $\omega = 2\pi n \frac{90^\circ}{\alpha}$ ,  $n$  being the r.p.s. of the armature. When the armature moves from  $\theta = -90^\circ$  at  $A$  to  $\theta$  at  $B$ , there is no change of flux through it, and therefore no current will flow in the primary winding. From  $B$  to  $C$ , however, there is a variation in flux, and we have the following relation:

$$L \frac{di}{dt} + Ri = E = nN_1 \frac{d \cos \omega t}{dt} \\ = -\omega nN_1 \sin \omega t,$$

where  $R$  and  $L$  are assumed constant. The solution of

this equation is given by

$$i = \frac{\omega n N_1}{(R^2 + \omega^2 L^2)^{\frac{1}{2}}} \cos \left[ \omega t - \tan^{-1} \frac{\omega L}{R} \right] - \frac{\omega n N_1 R}{R^2 + \omega^2 L^2} e^{-\frac{Rt}{L}}, \quad (20)$$

where  $\omega$  = angular velocity corresponding to the rate of flux interlinkage along BOC due to rotation of the armature.

For given values of magnet flux  $N_1$ , armature turns  $n$ , effective resistance  $R$ , and inductance  $L$ , it can be shown from (20) that the current  $i$  for a definite value of  $\omega t$  ( $\theta$  on the curved portion) increases with  $\omega$ . Now in moving from B to C,  $\omega t$  is 180 electrical degrees\*; hence, for large current,  $\omega$  should be large, *i. e.* the slope from B to C should be steep, in order that the rate of flux interlinkage may be correspondingly rapid. It is obviously the energy loss due to the effective resistance that prevents the current attaining its full value. This means that at break the flux through the armature is less than that at make, owing to the lack of constraint caused by reduction in current—or, in other words, the flux is not fully distorted. Thus  $\omega L$  should be great in comparison with  $R$ , so that the  $i^2 R$  time integral  $[\int i^2 R dt = \text{energy lost}]$  is small. For low speeds this would necessitate a large value of  $\omega$ —that is, a steep slope at BC. In the limit when  $\omega = \infty$ , BC is perpendicular to the  $\theta$  axis and the flux curve is truly rectangular. If this condition could obtain in practice, the current in an armature of finite effective resistance  $R$  would attain its full value at break whatever the speed of rotation, provided it was not zero. Thus, in the actual machine, we conclude that for meritorious performance at low speeds, the effective resistance (chiefly ohmic copper loss) should be small and the flux curve as nearly rectangular as possible. The latter criterion involves a very rapid increase in reluctance of the circuit external to the magneto in the neighbourhood of the ignition point. In practice, where the timing is variable as a rule, it is essential, in order to carry out this suggestion, that the flux curve should be bodily retarded or advanced according to the point of break. In a certain class of magneto the effect is simulated approximately by varying the configuration of the magnetic circuit external to the magnet, thus altering the flux distribution for different angular positions relative to mid-position. The variation generally occurs at the pole tips, these being movable; but from a practical, and certainly from a commercial viewpoint, it is hardly worth the additional complications and

\* Or, more concisely,  $\theta = \pi/2\omega$ .

expense. In the ideal case as cited above, the rate of flux cutting should be equal for all timing positions and should be extremely high. A magneto fitted with variable pole-tips falls short of the hypothetical case, the discrepancy naturally being most marked at slow speeds.

We will now tabulate the preceding argument in symbolical form, using equation (20) :

$$i = \frac{\omega n N_1}{(R^2 + \omega^2 L^2)^{\frac{1}{2}}} \left[ \cos(\omega t - \alpha) - \frac{R}{(R^2 + \omega^2 L^2)^{\frac{1}{2}}} e^{-\frac{Rt}{L}} \right].$$

A. At very low speed, when  $R \geq \omega L$ , we obtain

$$i \doteq \frac{\omega n N_1}{R} \cos \omega t = \frac{E}{R}, \quad . . . . . (21)$$

where  $E$  = induced e.m.f.

Thus Ohm's law holds, and the current and voltage waves are almost similar in shape simultaneously. Clearly the value of  $R$  should be as small as possible, other factors, such as contact breaker sparking at high speeds, being taken into account in fixing its value.

B. At high speed (when the current is independent of speed)  $\omega L \geq R$ , and we get

$$i = \frac{\omega n N_1}{\omega L} \cos \left( \omega t - \frac{\pi}{2} \right) = \frac{n N_1}{L} \sin \omega t = \frac{n N_1}{L} \sin \theta. \quad (22)$$

C. At break \* in case (A), the current at break,

$$I_B = \frac{\omega n N_1}{R} \quad . . . . . (23)$$

(dependent on speed).

D. At break in case (B), the current at break,

$$I_B = \frac{n N_1}{L} \quad . . . . . (24)$$

(independent of speed).

E. The "decrease" in current at low speed, due to resistance  $R$ , is approximately

$$\frac{n N_1}{L} - \frac{\omega n N_1}{R} = n N_1 \left[ \frac{1}{L} - \frac{\omega}{R} \right]. \quad . . . (25)$$

\*  $\theta = 90^\circ$  in this instance.

As  $\omega$  increases, the quantity in brackets tends to zero, assuming  $L$  and  $R$  to remain constant. This equation is only approximate, and if we take the limiting case where the bracket is zero,  $\omega L = R$ . This does not mean that the full value of the current is attained when  $\omega L = R$ ; the equation can be interpreted by saying that, were  $\omega L = R$  for all speeds of rotation,  $R$  and the ignition-point being fixed, the current at break would always be the same. In each case terms involving the exponential  $e^{-R/L}$  have been neglected, and from an analytical standpoint it is well to remember that these equations are not rigorous, and are merely intended to show in a simple manner the influence of resistance. These remarks apply with equal force to the energy equations about to be given.

F. Energy at break (mid-position) in case (C)

$$W = \frac{1}{2} L I_B^2 = \frac{1}{2} L \frac{\omega^2 n^2 N_1^2}{R^2}. \quad \dots \dots (26)$$

G. Energy at break in case (D)

$$= \frac{1}{2} L \frac{n^2 N_1^2}{L^2} = \frac{n^2 N_1^2}{L}. \quad \dots \dots (27)$$

H. Ratio of (28) to (29)

$$= \frac{\omega^2 L^2}{R^2}. \quad \dots \dots (28)$$

From (28) we again see that the energy is augmented by increase in speed and by decrease in resistance.

From the approximate equations deduced in this section, we are in a position to examine the problem of securing the optimum conditions when there is a loss of energy during rotation. At low speed we get from (26)

$$\text{Energy at break : } W = L \omega^2 n^2 N_1^2 / 2R^2.$$

For a given speed of rotation ( $\propto \omega$ ), armature turns  $n$ , and armature effective resistance  $R$  (chiefly cupric loss at low speed), if  $N_1$  is increased by reducing the air-gap and keeping the armature diameter constant, or by augmenting it so that the distance between the pole-faces is unaltered, the self-inductance  $L$  is increased and also the energy at break. The formula would clearly not apply when the air-gap was so small that  $L$  became numerically important compared with  $R$ . Thus we can, after a little consideration, see that with a certain magnet for any particular speed of

rotation there is (a) an optimum gap for a given armature, (b) an optimum armature diameter for given gap and armature length. Similarly, at any definite speed there is an optimum magnet\*, *i. e.* one for which the magneto energy per unit volume of magnet is a maximum. At high speed, where  $\omega L \gtrsim R$ , it is clear from (27) that the energy is independent of the speed, and its value does not differ very materially from the theoretical value. In this case the value of  $B$  on the auxiliary curve of fig. 7, for which the optimum condition was satisfied would be smaller than that at low speed, since it is desirable in the latter case to increase the flux through the armature, and therefore through the magnet. Moreover, the optimum gap or the optimum armature diameter decreases with reduction in speed, whilst the flux  $N_1$  increases.

An approximate method of determining the optimum magnet at the lowest running speed on full retard would be as follows:—Find the optimum magnet as shown herein when there is no loss, *i. e.* the armature effective resistance is zero and the air-gap is as small as possible mechanically. Then augment the length of the magnet by an amount best determined from experience. In practice it is known that the best procedure to adopt in securing satisfactory performance at low speeds is to make the air-gap as small as is possible mechanically.

#### *Conclusion.*

From a practical standpoint it is only the energy at slow speeds that matters, although the question of a highly advanced ignition for racing motors has to be considered also. As a general rule, if the energy at slow speeds is adequate, that at high speeds is adequate too. Resistance effects have not been introduced into the energy analysis associated with the hysteresis quadrant, as the treatment would be very cumbersome and unwieldy. The method just indicated for ascertaining the optimum magnet at slow speeds is probably sufficiently accurate to fulfil most practical requirements. Since the cost of magnet steel is not exorbitant, it is of minor importance if the magnet is slightly oversize. In many cases, if not all, the size of magnet can be determined (the exigencies of the situation sometimes demand that it shall be) empirically, but it is always desirable, if possible, to reduce design to an arithmetical basis.

\* Assuming the cross-sectional area to be fixed.

The problem of energy transfer from primary to secondary has not been discussed. The energy transformation and the proportion of the primary energy in the initial capacity spark is, for given numbers of turns and armature diameter, chiefly a question of the coefficient of coupling between the two windings. The smaller the air-gap, the greater this coefficient. In the induction-coil there is an optimum coupling, *i.e.* one which gives the greatest secondary peak voltage for a given current broken in the primary; but in the magneto the optimum is not so marked owing to the large iron loss, although it exists. At low speed the effect of resistance, as we have shown already, demands a small air-gap and therefore a close coupling to obtain sufficient primary current at break. Moreover, in this case, where an appreciable proportion of the energy is dissipated in heat in the armature prior to break, the optimum coupling involves not only the relation between the primary and secondary circuits, but also the value of the primary current at break. The optimum magnet in this case would be one for which the electrostatic energy in the spark ( $\frac{1}{2}C_2V_2^2$ ) per unit volume of magnet was a maximum\*. Since  $C_2$  is assumed fixed, it is clear that  $V_2$  should be a maximum. This introduces a problem of much greater magnitude and complexity than we have contemplated hitherto, and it is not proposed to pursue the subject any further at present.

We may close with the following summary of salient deductions:—

- (1) In the absence of loss or at high speeds where the armature current is constant: (a) with an armature and magnet of prescribed dimensions, there is a certain air-gap for which the electromagnetic energy associated with the primary winding at break is a maximum. The optimum point for the magnet is not situated on the main hysteresis loop, but on an auxiliary curve which is the intersection of subsidiary lines and armature reluctance curves: (b) when the dimensions of armature, air-gap, and magnet section are fixed, there is a certain length of magnet for which the energy associated with the primary at break per unit volume of magnet is a maximum.

\* Assuming ignition depends entirely on the capacity component of the spark. In cold weather it appears that the inductive component plays an equally important part when the mixture is improperly vaporized.

- (2) In the actual machine (where loss occurs) at low speeds of rotation, conclusions (a) and (b) are valid, but the optima values vary with the speed.
- (3) For meritorious performance at low speeds on retard, the air-gap should be as small as is mechanically possible. Also the primary resistance (ohmic chiefly) should be as small as is compatible with satisfactory operation and freedom from contact-breaker sparking at high speeds.

XXXVIII. *Orbits in the Field of a Doublet, and generally of Two Centres of Force.* By Sir G. GREENHILL \*.

THE orbit in the field of a magnetic molecule doublet, discussed by Dr. D. Wrinch in the *Phil. Mag.* May 1922, is a special case of Euler's problem (1760) of the path of a particle in the gravity field of the attraction or repulsion of two fixed spheres. A subsequent discussion is carried out at great length in Legendre's *Fonctions elliptiques*, i. p. 411, to the extent of 150 pages.

1. Resuming the investigation given on the "Stability of Orbits," *Proceedings of the London Math. Society (L.M.S.)* xxi. 1888, the motion is referred to the coordinates  $\phi, \theta$  on the Weir Azimuth Chart, defined by the conformal representation

$$x + iy = c \operatorname{ch}(\phi + i\theta), \quad x = c \operatorname{ch} \phi \cos \theta, \quad y = c \operatorname{sh} \phi \sin \theta, \quad . \quad (1)$$

$$\frac{x^2}{c^2 \operatorname{ch}^2 \phi} + \frac{y^2}{c^2 \operatorname{sh}^2 \phi} = 1, \quad \frac{x^2}{c^2 \cos^2 \theta} - \frac{y^2}{c^2 \sin^2 \theta} = 1, \quad . \quad (2)$$

a system of confocals, such that  $\phi$  is constant along the confocal ellipse,  $\theta$  along the confocal hyperbola, with foci at S, S',  $x = \pm c, y = 0$ ; and with  $r, s$  the focal distance SP, S'P of a point P

$$r, s = c(\operatorname{ch} \phi \mp \cos \theta). \quad . \quad . \quad . \quad (3)$$

The potential function (P.F.) of two Newtonian centres of force at S, S' is written

$$U = U_1 + U_2, \quad U_1 = \frac{Ac^3}{r}, \quad U_2 = \frac{Bc^3}{s}; \quad . \quad . \quad . \quad (4)$$

so that if  $U_1$  is the P.F. of a sphere of radius  $c$ , density  $\rho$ , and centre at S,  $A = \frac{4}{3}\pi G\rho = \omega^2$ , where  $\omega$  is the angular velocity of a satellite grazing the surface of the sphere.

\* Communicated by the Author.

The kinetic energy (K.E.) of unit particle

$$\begin{aligned} \frac{1}{2}v^2 &= \frac{1}{2}\left(\frac{dx}{dt}\right)^2 + \frac{1}{2}\left(\frac{dy}{dt}\right)^2 = \frac{1}{2}c^2(\text{sh } \phi \cos \theta \phi' - \text{ch } \phi \sin \theta \theta')^2 \\ &\quad + \frac{1}{2}c^2(\text{ch } \phi \sin \theta \phi' + \text{sh } \phi \cos \theta \theta')^2 \\ &= \frac{1}{2}c^2(\text{ch}^2 \phi - \cos^2 \theta)(\phi'^2 + \theta'^2), \quad (5) \end{aligned}$$

and then the Energy Equation may be written

$$\begin{aligned} \frac{1}{2}(\text{ch}^2 \phi - \cos^2 \theta)(\phi'^2 + \theta'^2) \\ = \frac{A}{\text{ch } \phi - \cos \theta} + \frac{B}{\text{ch } \phi + \cos \theta} + H, \quad (6) \end{aligned}$$

and H is negative if the orbit does not stretch to infinity.

2. Euler's second integral can be obtained in a more general form by introducing the stream-function (S.F.) V, orthogonal to a (P.F.) U, defined by

$$\frac{dV}{dx} = y \frac{dU}{dy}, \quad \frac{dV}{dy} = -y \frac{dU}{dx},$$

or

$$\frac{dV}{d\phi} = y \frac{dU}{d\theta}, \quad \frac{dV}{d\theta} = -y \frac{dU}{d\phi}, \quad (1)$$

in the elliptic orthogonal coordinates,  $\phi, \theta$ ; or any other orthogonal pair.

Then if  $h, h'$  denote the angular momentum (A.M.) of unit particle at P about S, S';  $U_1, U_2$  a P.F. of a radial field of force from S, S', and  $V_1, V_2$  their S.F.; also  $\chi, \psi, \omega$  denoting the angles SPS', S'SP, SS'P, so that

$$h = -r^2 \frac{d\psi}{dt}, \quad h' = s^2 \frac{d\omega}{dt}; \quad \text{then with } \frac{dU}{ds} = \frac{1}{y} \frac{dV}{s d\omega},$$

$\frac{1}{r} \frac{dh}{dt}$  = resolved force of compound field perpendicular to SP

$$= \frac{dU_2}{ds} \sin \chi = \frac{1}{y} \frac{dV_2}{s d\omega} \sin \chi. \quad (2)$$

$$h' \frac{dh}{dt} = \frac{rs \sin \chi}{y} \frac{dV_2}{dt} = 2c \frac{dV_2}{dt}; \quad (3)$$

and similarly

$$h \frac{dh'}{dt} = -2c \frac{dV_1}{dt}, \quad \frac{1}{2} \frac{dhh'}{dt} = -c \frac{dV_1}{dt} + c \frac{dV_2}{dt}, \quad (4)$$

$$\frac{1}{2} h h' = -c V_1 + c V_2 + K', \quad K' = Kc^4, \quad (5)$$

the Action equation.



Thus if  $p, p'$  is the perpendicular from  $S, S'$  on the tangent of the orbit,

$$pp' = \frac{hh'}{v^2} = \frac{-cV_1 + cV_2 + K'}{U_1 + U_2 + H'} \dots \dots (6)$$

the general geometrical relation.

The Energy is constant along a line of constant P.F., and the Action is constant along an orthogonal line of force, S.F. constant.

Or the P.F. gives lines of equal Energy, and the S.F. gives orthogonal lines of force of equal Action (Maupertuis).

3. In Euler's problem of the two Newtonian central fields of force, about  $S, S'$ ,

$$U_1 = \frac{Ac^3}{r}, \quad V_1 = Ac^3 \cos \psi, \quad U_2 = \frac{Bc^3}{s}, \quad V_2 = -Bc^3 \cos \omega, \quad (1)$$

$$\frac{1}{2}hh' = -Ac^4 \cos \psi - Bc^4 \cos \omega + Kc^4; \quad \dots \quad (2)$$

and with the elliptic coordinates  $\phi, \theta$ ,

$$\cos \psi = \frac{1 - \operatorname{ch} \phi \cos \theta}{\operatorname{ch} \phi - \cos \theta}, \quad \cos \omega = \frac{1 + \operatorname{ch} \phi \cos \theta}{\operatorname{ch} \phi + \cos \theta}, \quad \dots \quad (3)$$

$$h = (x - c)y^* - yx^* = c^2(\operatorname{ch} \phi - \cos \theta)(\operatorname{sh} \phi \theta^* - \sin \theta \phi^*)$$

$$= -r^2 \frac{d\psi}{dt}, \quad \dots \dots \dots (4)$$

$$h' = (x + c)y^* - yx^* = c^2(\operatorname{ch} \phi + \cos \theta)(\operatorname{sh} \phi \theta^* + \sin \theta \phi^*)$$

$$= s^2 \frac{d\omega}{dt}, \quad \dots \dots \dots (5)$$

$$\frac{\frac{1}{2}hh'}{c^4} = \frac{1}{2}(\operatorname{ch}^2 \phi - \cos^2 \theta)(\operatorname{sh}^2 \phi \theta^{*2} - \sin^2 \theta \phi^{*2})$$

$$= -A \frac{1 - \operatorname{ch} \phi \cos \theta}{\operatorname{ch} \phi - \cos \theta} - B \frac{1 + \operatorname{ch} \phi \cos \theta}{\operatorname{ch} \phi + \cos \theta} + K, \quad \dots \quad (6)$$

and this is Euler's Second Integral, to be translated in Maupertuis' Principle of Action.

By a happy accident Euler found the variables could be separated in his special problem into the equations

$$\frac{1}{2}(\operatorname{ch}^2 \phi - \cos^2 \theta)^2 \phi^{*2} = H \operatorname{ch}^2 \phi + (A + B) \operatorname{ch} \phi - H - K, \quad (7)$$

$$\frac{1}{2}(\operatorname{ch}^2 \phi - \cos^2 \theta)^2 \theta^{*2} = -H \cos^2 \theta + (A - B) \cos \theta + H + K, \quad (8)$$

$$\begin{aligned} \frac{2dt^2}{(\operatorname{ch}^2 \phi - \cos^2 \theta)^2} &= \frac{d\phi^2}{H \operatorname{ch}^2 \phi + (A + B) \operatorname{ch} \phi - H - K} \\ &= dT^2 = \frac{d\theta^2}{-H \cos^2 \theta + (A - B) \cos \theta + H + K}, \quad (9) \end{aligned}$$

where the variables are seen separated, but this separation is

exceptional for the particular law of two fixed centres of gravitating force ; and writing

$$\begin{aligned}\Phi &\text{ for } H \operatorname{ch}^2 \phi + (A+B) \operatorname{ch} \phi - H - K, \\ \Theta &\text{ for } -H \cos^2 \theta + (A-B) \cos \theta + H + K, \quad (10)\end{aligned}$$

the integrals  $\frac{d\phi}{\sqrt{\Phi}}$  and  $\frac{d\theta}{\sqrt{\Theta}}$  are seen to be elliptic integrals ; and A, B, H, K are of the dimensions of  $\omega^2$ , or  $-2$  in time.

4. A centre of attraction varying as the distance may, however, be introduced at O, and the variables can still be separated. For writing its P.F.

$$\frac{1}{2}C(x^2 + y^2) = \frac{1}{2}C^2(\operatorname{ch}^2 \phi - \sin^2 \theta),$$

to be added to U, requires the addition to V of

$$-\frac{1}{2}C^2 \operatorname{sh}^2 \phi \sin^2 \theta = -\frac{1}{2}Cy^2 ;$$

and this adds

$$\frac{1}{2}C \operatorname{sh}^2 \phi \operatorname{ch}^2 \phi \text{ to } \Phi \text{ and } \frac{1}{2}C \sin^2 \theta \cos^2 \theta \text{ to } \Theta.$$

But the further integration becomes hyperelliptic and intractable.

And the addition to U of a term  $gx = gc \operatorname{ch} \phi \cos \theta$ , to represent a uniform gravity field in the direction SS', does not lead to a separation of the variables, and further progress is impracticable.

The S.F.  $-\frac{1}{2}Cy^2$  corresponds to a P.F.  $Cx$ , of a uniform field C ; but  $\frac{1}{2}C(x^2 + y^2)$  is not to be associated as a P.F.

5. Euler employs new variables  $u, v$ , which are found to be our  $\tan \frac{1}{2}\theta$ ,  $\operatorname{th} \frac{1}{2}\phi$  ; and his  $p, q$  are our  $c \cos \theta$ ,  $c \operatorname{ch} \phi$  (*Mémoires de Berlin*, 1760).

We shall follow Legendre's notation where  $p, q$  are used to denote  $\operatorname{th} \frac{1}{2}\phi$ ,  $\tan \frac{1}{2}\theta$  ; and then

$$\begin{aligned}\tan \frac{1}{2}\psi &= \cot \frac{1}{2}ASP = \frac{p}{q}, \quad \tan \frac{1}{2}\omega = \tan \frac{1}{2}AS'P = pq, \\ \operatorname{ch} \phi &= \frac{1+p^2}{1-p^2}, \quad \operatorname{sh} \phi = \frac{2p}{1-p^2}, \quad d\phi = \frac{2dp}{1-p^2}, \\ \cos \theta &= \frac{1-q^2}{1+q^2}, \quad \sin \theta = \frac{2q}{1+q^2}, \quad d\theta = \frac{2dq}{1+q^2}, \quad (1)\end{aligned}$$

$$\frac{d\phi}{\sqrt{\Phi}} = \frac{2dp}{\sqrt{P'}}, \quad \frac{d\theta}{\sqrt{\Theta}} = \frac{2dq}{\sqrt{Q'}},$$

$$\begin{aligned}P' &= H(1+p^2)^2 + (A+B)(1-p^4) - (H+K)(1-p^2)^2 \\ &= -(K+A+B)p^4 + 2(2H+K)p^2 - K + A + B,\end{aligned}$$

$$\begin{aligned}Q' &= -H(1-q^2)^2 + (A-B)(1-q^4) + (H+K)(1+q^2)^2 \\ &= (K-A+B)q^4 + 2(2H+K)q^2 + K + A - B, \quad (2)\end{aligned}$$

and thus with time  $t = t_1 + t_2$ , we can write

$$dt = (\text{ch}^2 \phi - \cos^2 \theta) \left( \frac{d\phi}{\sqrt{2\Phi}} \text{ or } \frac{d\theta}{\sqrt{2\Theta}} \right) \\ = \frac{\text{sh}^2 \phi d\phi}{\sqrt{2\Phi}} + \frac{\sin^2 \theta d\theta}{\sqrt{2\Theta}} = dt_1 + dt_2, \quad \dots (3)$$

$$dt_1 = \frac{\text{sh}^2 \phi d\phi}{\sqrt{2\Phi}} = \frac{8\rho^2}{(1-\rho^2)^2} \frac{d\rho}{\sqrt{2P'}}, \\ dt_2 = \frac{\sin^2 \theta d\theta}{\sqrt{2\Theta}} = \frac{8q^2}{(1+q^2)^2} \frac{dq}{\sqrt{2Q'}}, \quad \dots (4)$$

in which again the variables are separated, and  $t_1, t_2$  depend on elliptic integrals of the First, Second, and Third kind (E.I., I, II, III), as well as an algebraical term, where previous experience guides us to a form

$$\frac{2\rho\sqrt{P'}}{1-\rho^2} \text{ or } \text{th } \frac{1}{2}\phi\sqrt{\Phi} \text{ in } t_1 \\ \text{and } \frac{2q\sqrt{Q'}}{1+q^2} \text{ or } \tan \frac{1}{2}\theta\sqrt{\Theta} \text{ in } t_2; \quad \dots (5)$$

and when these are removed, we are left with elliptic integrals alone, as in § 17.

Legendre devotes 125 pages more to a discussion and classification of the different cases that can arise of the orbits, and appears to have lighted incidentally on the theory of Transformation.

It would lead too far to attempt to follow Legendre; but a start can be made on the elliptic or hyperbolic orbit, or a portion of it, described under the two centres of force; and in the case where the orbit is unstable, we can follow up the shape of the orbit as it falls away from the unstable path, or approaches it again asymptotically.

An investigation of the Stability of such an orbit was given in Proc. L. M. S. 1888, when the conditions were adjusted so that an ellipse or hyperbola was described, or a portion of the curve, employing the theorem that if the curve can be described under each centre of force separately, the same orbit can be described when both forces act, the squared velocity being then the sum (or difference) of the separate squared velocities.

6. In a complete ellipse,  $\phi = \beta$ , we find

$$P^2 = \left( \frac{d\phi}{dT} \right)^2 = \Phi = H \text{ch}^2 \phi + (A+B) \text{ch } \phi - H - K \\ = H(\text{ch } \phi - \text{ch } \beta)^2, \quad \dots (1)$$

with  $A + B = -2H \operatorname{ch} \beta$ , and  $H$  is negative, the motion stable.

In a complete branch of the hyperbola,  $\theta = \alpha$ ,

$$Q^2 = \left( \frac{d\theta}{dt} \right)^2 = \Theta = -H \cos^2 \theta + (A - B) \cos \theta + H + K \\ = -H(\cos \theta - \cos \alpha)^2, \quad \dots \quad (2)$$

with  $A - B = 2H \cos \alpha$ , and  $B$  negative, force at  $S'$  repelling; thus  $H$  is positive and the motion stable.

Reduce  $B$  to zero in the complete ellipse, and the motion is the ordinary planetary orbit; and reducing  $B$  still further to negative values, as in the hyperbolic branch, put  $B = -D$ .

When the forces are equal at aphelion from  $S$  of the ellipse, the breaking point is reached; and after that, as  $D$  is increased,  $\Theta$  can vanish, and an arc of the ellipse is described, provided the forces to  $S$  and from  $S'$  are equal at the breaking point of zero velocity, say  $\phi = \beta$ ,  $\theta = \alpha$ ; so that we can put

$$A = n^2(\operatorname{ch} \beta - \cos \alpha)^2, \quad D = n^2(\operatorname{ch} \beta + \cos \alpha)^2, \\ \Phi = n^2(\operatorname{ch} \phi - \operatorname{ch} \beta)^2, \quad \dots \quad (3)$$

with  $H + K = -H \operatorname{ch}^2 \beta$ ,  $A - D = -2H \operatorname{ch} \beta$ ,

$$H = 2n^2 \cos \alpha,$$

and the motion is unstable unless  $\cos \alpha$  is negative, and the larger half of the ellipse is described, with little or no play from  $\phi = \beta$ . Then

$$Q^2 = \left( \frac{d\theta}{dT} \right)^2 = \Theta = 2n^2(\cos \theta - \cos \alpha)(\operatorname{ch}^2 \beta - \cos \alpha \cos \theta), \quad (4)$$

giving  $\theta$  as an Elliptic Function (E.F.) of  $T$ , in the form

$$\tan \frac{1}{2}\theta = \tan \frac{1}{2}\alpha \operatorname{cn} mT. \quad \dots \quad (5)$$

So, too, under two centres of attraction at  $S, S'$ , a particle placed at rest where the two forces are equal, at  $(\phi, \alpha)$ , can oscillate on the arc of the hyperbola  $\theta = \alpha$ , with

$$\Theta = -H(\cos \theta - \cos \alpha)^2,$$

$$H + K = -H \cos^2 \alpha, \quad 2H \cos \alpha = A - B = -4n^2 \operatorname{ch} \beta \cos \alpha,$$

$$H = -2n^2 \operatorname{ch} \beta, \quad \dots \quad (6)$$

and the motion is unstable. And

$$P^2 = \left( \frac{d\phi}{dT} \right)^2 = \Phi = 2n^2(\operatorname{ch} \beta - \operatorname{ch} \phi)(\operatorname{ch} \beta \operatorname{ch} \phi - \cos^2 \alpha),$$

$$\operatorname{th} \frac{1}{2}\phi = \operatorname{th} \frac{1}{2}\beta \operatorname{cn} mT. \quad \dots \quad (7)$$

But if repelled from S, S' with the sign of A, B changed,

$$Q^2 = \left(\frac{d\theta}{dT}\right)^2 = \Theta = -2n^2 \operatorname{ch} \beta (\cos \theta - \cos \alpha)^2, \quad (8)$$

and the motion is stable along the hyperbolic arc reaching to infinity; with

$$P^2 = \left(\frac{d\phi}{dT}\right)^2 = \Phi = 2n^2 (\operatorname{ch} \phi - \operatorname{ch} \beta) (\operatorname{ch} \beta \operatorname{ch} \phi - \cos^2 \alpha), \quad (9)$$

$$\coth \frac{1}{2} \phi = \coth \frac{1}{2} \alpha \operatorname{cn} mT.$$

With the stability examined otherwise, from

$$\frac{dQ}{dT} = \frac{d\Theta}{2d\theta},$$

$$\frac{d^2Q}{dT^2} = -2n^2 \operatorname{ch} \beta (\sin^2 \theta - \cos^2 \theta + \cos \alpha \cos \theta)$$

$$= -2n^2 \operatorname{ch} \beta \sin^2 \alpha \dots \dots \dots (10)$$

along  $\theta = \alpha$ ; here Q can fluctuate slightly between close limits, and the motion is stable.

A further discussion will be found in the Proc. London Math. Society, vol. xxii., 1888, "Stability of Orbits."

7. Putting  $A + B = 0$  in the general case introduces some simplification into the integrals, making  $\Phi = H \operatorname{sh}^2 \phi - K$ , and gives the field of force of a bar magnet along SS'.

Thus if a particle is placed at rest anywhere on the line Oy where the forces are equal, it will proceed to oscillate in a semi-ellipse,  $\phi = \beta$ , with  $\Phi = 0$ ; and then, if

$$A = -B = \frac{1}{2}\omega^2, \quad A - B = \omega^2,$$

$$\frac{1}{2}(\operatorname{ch}^2 \beta - \cos^2 \theta)^2 \left(\frac{d\theta}{dt}\right)^2 = \Theta = \omega^2 \cos \theta, \quad (1)$$

$$\omega t = \int (\operatorname{ch}^2 \beta - \cos^2 \theta) \sqrt{2 \cos \theta} \cdot \dots \dots (2)$$

An algebraical term Z can be set aside, where

$$Z = \frac{1}{3} \sin \theta \sqrt{2 \cos \theta}, \quad \frac{dZ}{d\theta} = \frac{\cos^2 \theta}{\sqrt{2 \cos \theta}} - \frac{1}{3} \frac{1}{\sqrt{2 \cos \theta}}. \quad (3)$$

and then

$$\omega t = (\operatorname{ch}^2 \beta - \frac{1}{3}) \int \frac{d\theta}{\sqrt{2 \cos \theta}} - Z, \quad (4)$$

in which

$$\int \frac{d\theta}{\sqrt{2 \cos \theta}} = \operatorname{cn}^{-1} \sqrt{\cos \theta}, \quad (5)$$

to a lemniscate modular angle  $45^\circ$ .

The analogous case can be considered when the velocity is due to a twin vortex, at S, S'; and the orbits are circles or Cassinians, as of a cyclone, tornado, habbab, waterspout, air whirl, dust column, will o' the wisp, friar's lantern.

8. With  $H=0$ , so that the velocity is zero at infinity, then as in the restriction of pendulum motion,

I. $A+B > K$ .	II. $A+B < K$ .
(1) $\Phi = (A+B) \operatorname{ch} \frac{1}{2} \phi - K$ $= (A+B+K) \operatorname{sh}^2 \frac{1}{2} \phi$ $+ (A+B-K) \operatorname{ch}^2 \frac{1}{2} \phi$ $= (A+B+K) \frac{\operatorname{dn}^2 u}{\kappa^2 \operatorname{sn}^2 u}$	$= (K+A+B) \operatorname{sh}^2 \frac{1}{2} \phi$ $- (K-A-B) \operatorname{ch}^2 \frac{1}{2} \phi$ $= (K+A+B) \frac{\operatorname{cn}^2 u}{\operatorname{sn}^2 u}$
(2) $\operatorname{th} \frac{1}{2} \phi = \operatorname{cn} u$ $\operatorname{ch} \frac{1}{2} \phi = \frac{1}{\operatorname{sn} u}$ $\operatorname{sh} \frac{1}{2} \phi = \frac{\operatorname{cn} u}{\operatorname{sn} u}$ $d\phi = - \frac{2 \operatorname{dn} u du}{\operatorname{sn} u}$ $\kappa^2 = \frac{A+B+K}{2A+2B}$	$= \operatorname{dn} u$ $= \frac{1}{\kappa \operatorname{sn} u}$ $= \frac{\operatorname{dn} u}{\kappa \operatorname{sn} u}$ $= - \frac{2 \operatorname{cn} u du}{\operatorname{sn} u}$ $= \frac{2A+2B}{K+A+B}$
(3) $dT = \frac{d\phi}{\sqrt{\Phi}} = - \frac{2\kappa du}{\sqrt{(A+B+K)}}$	$= \frac{-2du}{\sqrt{(K+A+B)}}$

And as in pendulum motion,

$\theta$ oscillating.	$\theta$ circulating.
(4) $\Theta = (A-B) \cos \theta + K$ $= (A-B+K) \cos^2 \frac{1}{2} \theta$ $- (A-B-K) \sin^2 \frac{1}{2} \theta$ $= (A-B+K) \operatorname{cn}^2 v$	$= (K+A-B) \cos^2 \frac{1}{2} \theta$ $+ (K-A+B) \sin^2 \frac{1}{2} \theta$ $= (K-A+B) \operatorname{dn}^2 v$
(5) $\cos \frac{1}{2} \theta = \operatorname{dn} v$ $\tan \frac{1}{2} \theta = \frac{\kappa}{\kappa'} \operatorname{cn} (K-v)$ $d\theta = 2\kappa \operatorname{cn} v dv$ $\kappa^2 = \frac{K+A-B}{2A-2B}$	$= \operatorname{cn} v$ $= \operatorname{tn} v$ $= 2 \operatorname{dn} v dv$ $= \frac{2A-2B}{K+A-B}$
(6) $dT = \frac{d\theta}{\sqrt{\Theta}} = \frac{2\kappa dv}{\sqrt{(A-B+K)}}$	$= \frac{2dv}{\sqrt{(K-A+B)}}$

In a further exploration when  $H$  is restored in  $\Theta$ , the effect in the associated pendulum is as if the axle was made

to revolve about a vertical axis on a whirling arm with angular velocity  $m$ , where  $H$  may be replaced by  $m^2$ , and the reduction of the various cases that arise is given in the Report on Gyroscopic Theory, p. 204 (1914), ranging from  $\tan \frac{1}{2}\theta = \tan \frac{1}{2}\alpha \operatorname{cn}(K-r)$  to  $\operatorname{th} \frac{1}{2}\beta \operatorname{tn} r$ .

A different shape of a compound pendulum can make  $H$  negative, and then  $H = -m^2$ .

This motion can be projected stereographically into free pendulum oscillation. And the  $\phi$  integral is reduced immediately to a preceding  $\theta$  form by the substitution

$$\operatorname{th} \frac{1}{2}\phi = \tan \frac{1}{2}\theta, \quad \operatorname{ch} \phi = \sec \theta, \quad d\phi = \sec \theta d\theta. \quad (7)$$

9. In the special field of the magnetic molecule at  $O$  considered by Dr. Wrinch, Phil. Mag. May 1922, where our  $c$  is zero, by the coalescence of  $S$  and  $S'$ , and the preceding analysis nugatory, replace Euler's results by

$x + iy = c \exp(\phi + i\theta), \quad x, y = ce^\phi(\cos \theta, \sin \theta), \quad r = ce^\phi, \quad (1)$   
equivalent to replacing  $\operatorname{ch} \phi, \operatorname{sh} \phi$  by  $e^\phi$ , and

$$U = c \left( -\frac{d}{dx} \right) \frac{Bc^3}{r} = B \frac{c^4 x}{r^3} = Bc^2 e^{-2\phi} \cos \theta,$$

$$V = Bc^3 \frac{y^2}{r^3} = Bc^3 e^{-\phi} \sin^2 \theta = B \frac{c^4}{r} \sin^2 \theta, \quad (2)$$

$$\frac{dV}{d\phi} = y \frac{dU}{d\theta}, \quad \frac{dV}{d\theta} = -y \frac{dU}{d\phi}. \quad (3)$$

Weir's Azimuth diagram is replaced here by concentric circles, of radius in G.P. for equal increments of  $\phi$ , and radiating lines at equal angular interval of  $\theta$ .

The work is essentially not more complicated if a centre of gravitation is introduced at  $O$ , as if the  $A$  sphere was magnetic as well as gravitating, making

$$U = Ac^2 e^{-\phi} + Bc^2 e^{-2\phi} \cos \theta = A \frac{c^3}{r} + B \frac{c^4}{r^2} \cos \theta,$$

$$V = -Ac^3 \cos \theta + Bc^3 e^{-\phi} \sin^2 \theta = -Ac^3 \cos \theta + B \frac{c^4}{r} \sin^2 \theta. \quad (4)$$

Then in the ordinary polar equations of motion, resolving transversely,

$$\frac{dh}{dt} = \frac{dU}{d\theta} = -Bc^2 e^{-2\phi} \cos \theta, \quad (5)$$

$$h \frac{d\theta}{dt} = -Bc^4 \sin \theta \frac{d\theta}{dt}, \quad \text{with } h = c^2 e^{2\phi} \frac{d\theta}{dt}. \quad (6)$$

and integrating

$$\frac{1}{2}h^2 = Bc^4 \cos \theta + Kc^4, \quad e^{-4\phi} dt^2 = \frac{d\theta^2}{2B \cos \theta + 2K}.$$





where

$$\frac{1}{2}\theta' = \sqrt{\left(\frac{K}{K+B}\right)} r = \sqrt{(1-\frac{1}{2}\kappa^2)} F(\frac{1}{2}\theta, \kappa), \kappa = \sqrt{\frac{2B}{K+B}}. \quad (2)$$

SA, SA' the perihelion and aphelion distance; and the apsidal angle is raised from  $\pi$  to  $2K\sqrt{(1-\frac{1}{2}\kappa^2)}$ .

This is somewhat analogous to the case of the Einstein orbit, where the addition of the term  $3mh^2u^4$  to  $\mu u^2$  changes the orbit from

$$\frac{1}{SP} = \frac{\cos^2 \frac{1}{2}\theta}{SA} + \frac{\sin^2 \frac{1}{2}\theta}{SA'} \text{ into } \frac{\text{cn}^2 \frac{1}{2}p\theta}{SA} + \frac{\text{sn}^2 \frac{1}{2}p\theta}{SA'} \quad (3)$$

(Phil. Mag. Jan. 1921).

11. The investigation of some possible orbits is carried out by Dr. Wrinch in the Phil. Mag., May 1922; also in August 1910, p. 380, by J. H. Jeans.

The curvilinear coordinates of the confocals on Weir's Azimuth Diagram can be employed in Perigal's manner of the construction of Lissajous figures of vibration, for the general case of two centres of force, tacking from one corner to the opposite of small curvilinear rectangles, taking the step in  $\phi$  and  $\theta$  in the ratio of  $d\phi$  or  $\sqrt{\Phi}$  and  $d\theta$  or  $\sqrt{\Theta}$ .

A standard orbit of this nature would be worth investigation as a useful Research, to add to those attempted by Legendre, utilising Elliptic Function Theory to obtain a closed figure.

A specimen orbit winding about inside a finite curvilinear rectangle would have the appearance of an analogous Lissajous figure of simple vibration contained in a plane rectangle of straight sides. These curves could be shown by a spot of light reflected from a pair of mirrors in vibration, with surfaces of appropriate curvature.

Putting  $B=0$  should reduce our orbit to a plane elliptic or hyperbolic orbit about the focus S. And if the conditions are adjusted to make S' the other focus, so that the orbit is given by  $\phi$  or  $\theta$  a constant, we notice that while the Time is given by the sector area round S, the Action is represented by the sector area round S'.

With  $B=0$ ,  $\Phi$  changes into  $-\Theta$  by the change of  $\text{ch } \phi$  into  $-\cos \theta$ , or  $P'$  into  $-Q'$  by a change of  $p^2$  into  $-q^2$ .

Thence the modulus  $\kappa$  is the same in the two elliptic integrals, and the orbit is given by the Algebraical Addition Theorem, in the form

$$r = Ax + By + C, \dots \dots \dots (1)$$

$$\text{or} \quad A \text{ch } \phi \cos \theta + B \text{sh } \phi \sin \theta + C - \text{ch } \phi + \cos \theta = 0. \dots (2)$$

12. If the body has a velocity communicated perpendicular to the plane SPS', it will describe an orbit in three-fold space; and referred to the plane SPS' revolving with angular velocity  $\frac{d\rho}{dt}$ , a first integral is  $y^2 \frac{d\rho}{dt} = \text{a constant}$ , which Legendre denotes by H. We replace his  $H^2$  by  $Dc^4$ , so that D is of the dimensions  $\omega^2$ , the same as our H, K, A, B.

No difference is made in the resolution of the motion parallel to SS'; but the effect of the rotation  $\frac{d\rho}{dt}$  is to diminish  $\frac{d^2y}{dt^2}$  by  $y \left(\frac{d\rho}{dt}\right)^2$  or  $D \frac{c^4}{y^3}$  in the resolution along MP, and so to add  $D \frac{c^4}{y^3} (x-c, x+c)$  to  $\frac{dh}{dt}, \frac{dh'}{dt}$  in (3), (4), § 2.

Thus  $\frac{dhh'}{dt}$  in (4) is increased by

$$\begin{aligned} & \frac{Dc^4}{y^3} (x-c) \left[ (x+c) \frac{dy}{dt} - y \frac{dx}{dt} \right] \\ & + \frac{Dc^4}{y^3} (x+c) \left[ (x-c) \frac{dy}{dt} - y \frac{dx}{dt} \right] \\ & = 2 \frac{Dc^4}{y^3} \left[ (x^2 - c^2) \frac{dy}{dt} - xy \frac{dx}{dt} \right] \\ & = - Dc^4 \frac{d}{dt} \frac{x^2 - c^2}{y^2} = Dc^4 \frac{d}{dt} \cot \psi \cot \omega, \quad (1) \end{aligned}$$

making the total in (4), § 2,

$$\frac{1}{2} hh' = -cV_1 + cV_2 + Kc^4 - Dc^4 \frac{x^2 - c^2}{y^2}. \quad (2)$$

At the same time a term  $\frac{1}{2} y^2 \left(\frac{d\rho}{dt}\right)^2 = \frac{Dc^4}{2y^2}$  must be added to the Energy in (5) § 1; and this changes (6) § 5, (6) § 6 into

$$\frac{1}{2} (ch^2 \phi - \cos^2 \theta) (\theta'^2 + \phi'^2) \\ = H + \frac{A}{ch \phi - \cos \theta} + \frac{B}{ch \phi + \cos \theta} - \frac{D}{2 sh^2 \phi \sin^2 \theta}, \quad (3)$$

$$\frac{1}{2} (ch^2 \phi - \cos^2 \theta) (sh^2 \phi \theta'^2 - \sin^2 \theta \phi'^2) =$$

$$\begin{aligned} & K - A \frac{1 - ch \phi \cos \theta}{ch \phi - \cos \theta} - B \frac{1 + ch \phi \cos \theta}{ch \phi + \cos \theta} \\ & - D \frac{ch^2 \phi \cos^2 \theta - 1}{sh^2 \phi \sin^2 \theta}; \quad (4) \end{aligned}$$

thence (7), (8) § 3 change to

$$\frac{1}{2}(\text{ch}^2 \phi - \cos^2 \theta)^2 \phi'^2 = \\ H \text{ch}^2 \phi + (A + B) \text{ch} \phi - H - K - \frac{1}{2} D \coth^2 \phi = \Phi, \quad (5)$$

$$\frac{1}{2}(\text{ch}^2 \phi - \cos^2 \theta)^2 \theta'^2 = \\ -H \cos^2 \theta + (A - B) \cos \theta + H + K - \frac{1}{2} D \cot^2 \theta = \Theta, \quad (6)$$

so that  $\frac{1}{2} D \coth^2 \phi$ ,  $\frac{1}{2} D \cot^2 \theta$  are to be subtracted from the former values of  $\Phi$ ,  $\Theta$ , and the variables can still be separated.

Legendre then puts  $\text{ch} \phi = u$ ,  $\cos \theta = z$ , and

$$\frac{dy}{\sqrt{\Phi}} = \frac{du}{\sqrt{U}},$$

$$U = H(u^2 - 1)^2 + (A + B)u(u^2 - 1) - K(u^2 - 1) - \frac{1}{2} D u^2, \quad (7)$$

$$\frac{d\theta}{\sqrt{\Theta}} = \frac{-dz}{\sqrt{Z}},$$

$$Z = H(z^2 - 1)^2 - (A - B)z(z^2 - 1) - K(z^2 - 1) - \frac{1}{2} D z^2, \quad (8)$$

and so the integrals are elliptic still. And

$$dt = (\text{ch}^2 \phi - \cos^2 \theta) \left( \frac{d\phi}{\sqrt{2\Phi}} \text{ or } \frac{d\theta}{\sqrt{2\Theta}} \right) = \frac{u^2 du}{\sqrt{2U}} + \frac{z^2 dz}{\sqrt{2Z}}, \quad (9)$$

$$d\rho = \sqrt{D} \frac{c^2}{y^2} dt = \sqrt{D} \frac{\text{sh}^2 \phi + \sin^2 \theta}{\text{sh}^2 \phi \sin^2 \theta} \left( \frac{d\phi}{\sqrt{2\Phi}} \text{ or } \frac{d\theta}{\sqrt{2\Theta}} \right) \\ = \frac{\sqrt{D} d\phi}{\text{sh}^2 \phi \sqrt{2\Phi}} + \frac{\sqrt{D} d\theta}{\sin^2 \theta \sqrt{2\Theta}} = \frac{\sqrt{D} du}{(u^2 - 1) \sqrt{2U}} + \frac{\sqrt{D} dz}{(z^2 - 1) \sqrt{2Z}}, \quad (10)$$

introducing the Elliptic Integral of the Third Kind.

A C term in the P.F U. in § 4 due to a central force at 0 varying as the distance will add  $\frac{1}{4} C(u^2 - 1)(2u^2 - 1)^2$  and  $\frac{1}{4} C(z^2 - 1)(2z^2 - 1)^2$  to U and Z, and the integrals are seen to become hyperelliptic.

13. In the extension to three-fold space of this compound field of gravity and magnetism, proceeding as before in § 9, resolving transversely

$$\frac{dh}{dt} = -Bc^2 e^{-2\theta} \sin \theta + D \frac{c^4 \cos \theta}{r^2 \sin^3 \theta}, \quad \dots \quad (1)$$

$$h \frac{d\theta}{dt} = -Bc^4 \sin \theta \frac{d\theta}{dt} + Dc^4 \frac{\cos \theta}{\sin^3 \theta} \frac{d\theta}{dt}, \quad \dots \quad (2)$$

$$\frac{1}{2} h^2 = Bc^4 \cos \theta + Kc^4 - \frac{1}{2} D \frac{c^4}{\sin^2 \theta}, \quad \dots \quad (3)$$

and in the Energy relation

$$\frac{1}{2}v^2 = \frac{1}{2}\left(\frac{dr}{dt}\right)^2 + \frac{h^2}{2r^2} + D\frac{c^4}{2y^2} = Hc^2 + A\frac{c^3}{r} + B\frac{c^4}{r^2}\cos\theta, \quad (4)$$

$$\frac{1}{2}\left(\frac{dr}{dt}\right)^2 = Hc^2 + A\frac{c^3}{r} - K\frac{c^4}{r^2}, \quad . . . . . (5)$$

the terms in B and D cancelling ; or with  $\frac{c}{r} = u$ ,

$$\frac{du}{\sqrt{(2H + 2Au - Ku^2)}} = u^2 dt = \frac{c^2 d\theta}{h}, \quad . . . (6)$$

while from (8), with  $\cos\theta = z$ ,

$$\frac{r^3}{c^4}\left(\frac{dz}{dt}\right)^2 = 2(Bz + K)(1 - z^2) - D. \quad . . . . (7)$$

In the planetary orbit,  $B=0$ ,  $h$  is constant, and  $D$  may be ignored.

Moving on the surface of a sphere, of radius

$$r=a, \quad \frac{dr}{dt}=0, \quad \text{when } Ha^2 + Aac - Kc^2=0,$$

and with  $\frac{dr}{dt}=R$ ,

$$\frac{1}{2}R^2 = Ha^2 + A\frac{c^3}{r} - K\frac{c^4}{r^2}, \quad \frac{dR}{dt} = -A\frac{c^3}{r^2} + 2K\frac{c^4}{r^3}. \quad (8)$$

$$\frac{1}{R}\frac{d^2R}{dt^2} = 2A\frac{c^3}{r^3} - 6K\frac{c^4}{r^4}, \quad . . . . . (9)$$

so that this motion is unstable unless  $2A\left(\frac{c}{a}\right)^3 - 6K\left(\frac{c}{a}\right)^4$  is negative, or  $Kc > \frac{1}{3}Aa$ , and then over the sphere

$$\left(\frac{a}{c}\right)^4\left(\frac{dz}{dt}\right)^2 = 2(Bz + K)(1 - z^2) - D, \quad . . . (10)$$

representing a Spherical Pendulum motion, and as a conical pendulum it will give a circular orbit to the body.

14. The extreme case may be mentioned where  $S'$  recedes to an infinite distance from  $S$  (L.M.S. 1888) and then changing to an origin at  $S$ , we write

$$\begin{aligned} x + iy &= \frac{1}{2}a(\phi + i\theta)^2, \\ x &= \frac{1}{2}a(\phi^2 - \theta^2), \quad y = a\phi\theta, \quad r = \frac{1}{2}a(\phi^2 + \theta^2). \quad . \quad (1) \end{aligned}$$

The gravity field of B away at S' is practically uniform near S, and

$$U = \frac{Aa^3}{r} - 2Bax = \frac{2Aa^2}{\phi^2 + \theta^2} - Ba^2(\phi^2 - \theta^2),$$

$$V = -Aa^3 \frac{\phi^2 - \theta^2}{\phi^2 + \theta^2} + Ba^3\phi^2\theta^2, \quad . \quad . \quad (2)$$

$$\frac{1}{2}(\phi^2 + \theta^2)(\phi^2 + \theta^2) = \frac{2A}{\phi^2 + \theta^2} - B(\phi^2 - \theta^2) + H, \quad . \quad (3)$$

$$\frac{1}{2}(\phi^2 + \theta^2)(\phi^2\theta^2 - \phi^2\theta^2) = -A \frac{\phi^2 - \theta^2}{\phi^2 + \theta^2} - B\phi^2\theta^2 + K, \quad . \quad (4)$$

$$\frac{1}{2}(\phi^2 + \theta^2)^2\phi^2 = -B\phi^4 + H\phi^2 + A + K = \Phi, \quad (5)$$

$$\frac{1}{2}(\phi^2 + \theta^2)^2\theta^2 = +B\theta^4 + H\theta^2 + A - K = \Theta, \quad (6)$$

and so the variables are separated ;

$$\frac{d\phi}{\sqrt{\Phi}} \pm \frac{d\theta}{\sqrt{\Theta}} = 0,$$

$$dt = dt_1 + dt_2 = \frac{\phi^2 d\phi}{\sqrt{2\Phi}} + \frac{\theta^2 d\theta}{\sqrt{2\Theta}} = \frac{u du}{2\sqrt{U}} + \frac{z dz}{2\sqrt{Z}}. \quad (7)$$

with  $u = \phi^2 = \frac{r+x}{a}$ ,  $z = \theta^2 = \frac{r-x}{a}$ ,  $r \pm y = \frac{1}{2}a(\phi \pm \theta)^2$  ;

confocal parabolas along  $\phi, \theta$  constant ; thus leading to elliptic integrals of the Legendre-Jacobi-Weierstrass form, to be identified with the integrals in § 5, with  $p$  replaced by  $\phi$ , and  $q$  by  $\theta$ .

The diagram here is covered with confocal parabolas, and an orbit can be constructed by tacking from one corner to the next of the curvilinear rectangles, ruled by parabolas of appropriate spacing. Thus with  $B=0$ ,  $H=0$ , the orbit is an oblique trajectory parabola.

15. A complete parabola,  $\phi = \beta$ , can be described, with

$$\Phi = -B(\phi^2 - \beta^2)^2, \quad H = 2B\beta^2, \quad A + K = -B\beta^4, \quad . \quad (1)$$

and the motion is stable if B is positive.

Described freely under each force separately, the  $\frac{1}{2}(\text{vel})^2$  is  $A \frac{a^3}{r}$  and  $2Bar$ , and their difference is then the actual  $\frac{1}{2}(\text{vel})^2$  of the orbit.

The parabola breaks at the vertex,  $\theta = 0$ , if  $A = K = -\frac{1}{2}B\beta^4$ , where the two forces are then equal and

opposite ; so that A and B are of opposite sign, and taking A negative, the orbit is stable in each half parabola.

If this orbit breaks at  $\theta = \alpha$ , where the forces are equal,

$$\Theta = B(\theta^2 - \alpha^2)(\theta^2 + \alpha^2 + 2\beta^2), \quad t = \int (\theta^2 + \alpha^2) \frac{d\theta}{\sqrt{2\Theta}},$$

introducing the E.I., I and II.

If B is positive,  $\alpha < \theta < \infty$ , along a parabolic arc, stretching to infinity, and in stable motion.

But  $\alpha > \theta > -\alpha$  if B is negative, and the oscillatory motion of  $\phi$  is unstable ; and with  $\phi = \beta \text{ th } pu$ ,  $\theta = \alpha \text{ cn } qu$ .

16. In general, with  $A - K = 0$  in a further exploration

$$\begin{aligned} \frac{d\theta}{\sqrt{\Theta}} &= \frac{d\theta}{\theta \sqrt{(B\theta^2 + H)}}, \\ \int \frac{d\theta}{\sqrt{\Theta}} &= \frac{1}{\sqrt{H}} \text{sh}^{-1} \sqrt{\frac{H}{B\theta^2}}, \text{ or } \frac{1}{\sqrt{(-H)}} \text{sin}^{-1} \sqrt{\frac{-H}{B\theta^2}} \\ &= \left( \frac{1}{\sqrt{H}} \text{ or } \frac{1}{\sqrt{-H}} \right) \frac{\text{ch}^{-1}}{\cos^{-1}} \sqrt{\frac{B\theta^2 + H}{B\theta^2}}; \quad (1) \end{aligned}$$

or with  $A - K$  not too large, and positive or negative,

$$A \sim K = Ba^2b^2,$$

$$\begin{aligned} \Theta &= (A - K) \left(1 + \frac{\theta^2}{a^2}\right) \left(1 + \frac{\theta^2}{b^2}\right), \text{ or } (K - A) \left(1 - \frac{\theta^2}{a^2}\right) \left(\frac{\theta^2}{b^2} - 1\right), \\ &= (A - K) \frac{\text{dn}^2 u}{\text{cn}^4 u}, \quad \text{or } (K - A) \frac{\kappa^4}{\kappa'^2} \text{sn}^2 u \text{cn}^2 u, \quad (2) \end{aligned}$$

$$\theta = a \text{tn } u, \quad a = b\kappa', \quad \text{or } \theta = a \text{dn } u, \quad b = a\kappa', \quad (3)$$

$$\int \frac{d\theta}{\sqrt{\Theta}} = \frac{u \sqrt{\kappa'}}{\sqrt{(B \cdot A - K)}}, \quad \text{or } \frac{u}{\sqrt{(B \cdot K - A)}}, \quad (4)$$

$$\begin{aligned} \Phi &= (A + K) \left(1 - \frac{\phi^2}{c^2}\right) \left(1 - \frac{\phi^2}{d^2}\right), \quad A + K = Bc^2d^2, \\ &= (A + K) \frac{\text{sn}^2 v \text{dn}^2 v}{\kappa'^2} = cd \sqrt{(B \cdot A + K)} \frac{\text{sn}^2 v \text{dn}^2 v}{\kappa'^2}, \quad (5) \end{aligned}$$

$$\int \frac{d\phi}{\sqrt{\Phi}} = \frac{v \sqrt{\kappa\kappa'}}{\sqrt{(B \cdot A + K)}} \quad (6)$$

So also with  $A + K$  zero or small.

17. In a further determination of a time integral in § 5, for  $t_1$  and  $t_2$ , and first for  $t_2$ , with  $\cos \theta = x$ ,

$$\sqrt{(2H)} dt_2 = \sqrt{\left( \frac{1-x^2}{-x^2 + \frac{A-B}{H}x + 1 + \frac{K}{H}} \right)} dx = \frac{dx}{\sqrt{y}}. \quad (1)$$

putting, in a Quadric Transformation,

$$y = \frac{-x^2 + \frac{A-B}{H}x + 1 + \frac{K}{H}}{1-x^2}, \quad y-1 = \frac{\frac{A-B}{H}x + \frac{K}{H}}{1-x^2}. \quad (2)$$

Solving this as a quadratic for  $x$ ,

$$(y-1)x^2 + \frac{A-B}{H}x - y + 1 + \frac{K}{H} = 0, \quad \dots \quad (3)$$

$$x = \frac{-\frac{A-B}{2H} + \sqrt{(y-y_1 \cdot y-y_2)}}{y-1}. \quad \dots \quad (4)$$

Here  $y_1, y_2$  are the turning points of  $y$ , corresponding to  $x_1, x_2$  of  $x$ ;

$$y_1 - y \cdot y_2 - y = (y-1) \left( y-1 - \frac{K}{H} \right) + \left( \frac{A-B}{2H} \right)^2, \\ y_1 - 1 \cdot y_2 - 1 = \left( \frac{A-B}{2H} \right)^2, \quad \dots \quad (5)$$

$$\frac{y-y_1}{1-y_1} = \frac{(x-x_1)^2}{1-x^2}, \quad \frac{y-y_2}{1-y_2} = \frac{(x-x_2)^2}{1-x^2}, \quad \dots \quad (6)$$

$$\frac{dx}{dy} = \frac{\sqrt{(y_1-1 \cdot y_2-1)}}{(y-1)^2} + \frac{2y-y_1-y_2}{(y-1)\sqrt{(4 \cdot y-y_1 \cdot y-y_2)}} \\ - \frac{\sqrt{(y-y_1 \cdot y-y_2)}}{(y-1)^2}. \quad \dots \quad (7)$$

Guided by § 5 we can infer an algebraical term  $Z$  to set aside in  $t_2$ , where with  $Y = 4 \cdot y - y_1 \cdot y - y_2 \cdot y - y_3$ , and  $y_3 = 0$ ,

$$Z = \frac{1}{2}\sqrt{Y}, \quad \frac{dZ}{dy} = \frac{-\frac{1}{2}\sqrt{Y}}{(y-1)^2} + \frac{3y^2 - 2(y_1 + y_2)y + y_1y_2}{(y-1)\sqrt{Y}}, \quad (8)$$

$$\sqrt{(2H)} \frac{dt_2}{dy} - \frac{dZ}{dy} = \frac{y_1-1 \cdot y_2-1}{(y-1)\sqrt{Y}} - \frac{y-1}{\sqrt{Y}} + \frac{\sqrt{(y_1-1 \cdot y_2-1)}}{(y-1)^2\sqrt{y}}. \quad \dots \quad (9)$$

$$\frac{2H}{A-B} [\sqrt{(2H)t_2-Z}] = \int \frac{\sqrt{(y_1-1) \cdot y_2-1}}{y-1} \frac{dy}{\sqrt{Y}} - \int \frac{y-1}{\sqrt{(y_1-1) \cdot y_2-1}} \frac{dy}{\sqrt{Y}} + \int \frac{dy}{(y-1)^2 \sqrt{Y}}, \quad (10)$$

Here the second integral depends on the E.I., I and II, and in the region  $\infty > y > y_1 > 1 > y_2$ ,

$$\int_{y_1, v_1}^{\infty} \frac{\sqrt{(y_1-y_2)} dy}{\sqrt{Y}} = u \text{ or } eK, K, \\ \int_{y_2}^1 \frac{\sqrt{(y_1-y_2)} dy}{\sqrt{Y}} = v \text{ or } fK, \quad . \quad . \quad . \quad (11)$$

to modulus  $\kappa^2 = \frac{y_2-y_3}{y_1-y_3} = \frac{y_2}{y_3}$ , and we take

$$y_1 = \frac{1}{\kappa^2 \operatorname{sn}^2 v}, \quad y = \frac{y_1}{\operatorname{sn}^2 u} = \frac{1}{\kappa^2 \operatorname{sn}^2 u \operatorname{sn}^2 v}, \quad y_2 = \frac{1}{\operatorname{sn}^2 v}, \\ y-y_1 = \frac{\operatorname{cn}^2 u}{\kappa^2 \operatorname{sn}^2 u \operatorname{sn}^2 v}, \quad y-y_2 = \frac{\operatorname{dn}^2 u}{\kappa^2 \operatorname{sn}^2 u \operatorname{sn}^2 v}, \\ \frac{y-y_1}{y-y_3} = \operatorname{cn}^2 u, \quad \frac{y-y_2}{y-y_3} = \operatorname{dn}^2 u, \quad . \quad . \quad . \quad (12)$$

and then the second integral in (10)

$$\int \frac{y-1}{\sqrt{(y_1-1) \cdot y_2-1}} \frac{dy}{\sqrt{Y}} = \frac{\kappa^2 \operatorname{sn}^3 v}{\operatorname{cn} v \operatorname{dn} v} \int \left( \frac{1}{\kappa^2 \operatorname{sn}^2 u \operatorname{sn}^2 v} - 1 \right) du \\ = \frac{\operatorname{sn} v}{\operatorname{cn} v \operatorname{dn} v} \int \frac{du}{\operatorname{sn}^2 u} - \frac{\kappa^2 \operatorname{sn}^3 v}{\operatorname{cn} v \operatorname{dn} v}. \quad (13)$$

$$\text{And with } \frac{d^2}{du^2} \log \operatorname{sn} u = \frac{d}{du} \frac{\operatorname{cn} u \operatorname{dn} u}{\operatorname{sn} u} = 1 - \operatorname{dn}^2 u - \frac{1}{\operatorname{sn}^2 u},$$

$$\int \frac{du}{\operatorname{sn}^2 u} = u - E \operatorname{am} u - \frac{\operatorname{sn} u \operatorname{dn} u}{\operatorname{sn} u}; \quad . \quad . \quad . \quad (14)$$

where, in the Jacobi notation,

$$E \operatorname{am} u = \frac{E}{K} u + \operatorname{zn} u, \quad \operatorname{zn} u = \frac{d}{du} \log \Theta u$$

is Jacobi's zeta function,  $\operatorname{Zn} u$ ; and further

$$\operatorname{zs} u = \frac{d}{du} \log H u = \operatorname{zn} u + \frac{\operatorname{cn} u \operatorname{dn} u}{\operatorname{sn} u}, \\ \operatorname{zs}(K-v) = \operatorname{zn}(K-v) + \frac{\operatorname{cn}(K-v) \operatorname{dn}(K-v)}{\operatorname{sn}(K-v)} \\ = -\operatorname{zn} v + \frac{\operatorname{sn} v \operatorname{dn} v}{\operatorname{cn} v}. \quad . \quad . \quad . \quad (15)$$



The second integral in (10) thus adds up to

$$u \left( \frac{\text{sn } r}{\text{cn } v \text{ dn } v} - \frac{\kappa^2 \text{sn}^3 v}{\text{cn } v \text{ dn } v} \right) - \frac{\text{sn } v}{\text{cn } v \text{ dn } v} \left( \frac{E}{K} u + \text{zn } u + \frac{\text{cn } u \text{ dn } u}{\text{sn } u} \right) \\ = u \frac{\text{sn } v \text{ dn } v}{\text{cn } v} - \frac{\text{sn } v}{\text{cn } v \text{ dn } v} \left( \frac{E}{K} u + \text{zs } u \right). \quad (16)$$

The first integral in (10) is already in the standard form of  $\Pi$ , Jacobi's E.I. III,

$$\Pi = \int_0^u \frac{\kappa^2 \text{sn } v \text{ cn } v \text{ dn } v \text{ sn}^2 u \text{ du}}{1 - \kappa^2 \text{sn}^2 u \text{ sn}^2 v} = u \text{zn } v + \frac{1}{2} \log \frac{\Theta(v-u)}{\Theta(v+u)}, \quad (17)$$

and then the first and second integral in (10) make up

$$\frac{1}{2} \log \frac{\Theta(v-u)}{\Theta(v+u)} - u \text{zs } (K-v) + \frac{\text{sn } v}{\text{cn } v \text{ dn } v} \left( \frac{E}{K} u + \text{zs } u \right). \quad (18)$$

Finally the third integral is elementary

$$\int \frac{dy}{(y-1)^2 \sqrt{y}} = \frac{1}{2} \log \frac{\sqrt{y+1}}{\sqrt{y-1}} - \frac{\sqrt{y}}{y-1} \quad (19)$$

and the term in (10)

$$\frac{2\text{HZ}}{A-B} = \sqrt{\left( \frac{y-y_1 \cdot y-y_2}{y_1-1 \cdot y_2-1} \right) \frac{\sqrt{y}}{y-1}}, \quad (20)$$

so that, in all,

$$\frac{2\text{H}}{A-B} \sqrt{(2\text{H})t_2} = \log \frac{\Theta v \Theta u + \text{HvHu}}{\Theta 0 \Theta(v+u)} \\ - u \text{zs } (K-v) + \frac{\text{sn } v}{\text{cn } v \text{ dn } v} \left( \frac{E}{K} u + \text{zs } u \right) \\ + \left( \frac{\text{cn } u \text{ dn } u}{\kappa^2 \text{sn}^2 u \text{ cn } v \text{ dn } v} - 1 \right) \frac{\kappa \text{sn } u \text{ sn } v}{1 - \kappa^2 \text{sn}^2 u \text{ sn}^2 v}. \quad (21)$$

18. In the degenerate case of  $A=B$ ,

$$y-1 = \frac{K}{1-x^2}, \quad y_2 = 1, \quad y_1 = 1 + \frac{K}{H}, \quad \frac{K}{H} = y_1 - y_2 = \frac{\kappa'^2}{\kappa^2}, \quad (1)$$

$$x = \sqrt{\frac{y-y_1}{y-y_2}} = \frac{\text{cn } u}{\text{dn } u} = \text{sn}(K-u), \\ \frac{dx}{dy} = \frac{y_1-y_2}{(y-y_2) \sqrt{(4-y-y_1 \cdot y-y_2)}}, \quad (2)$$

$$\sqrt{(2H)}dt_2 = \frac{dx}{\sqrt{y}} = \frac{y_1 - y_2}{y - y_2} \frac{dx}{\sqrt{Y}}, \quad . . . . (3)$$

with  $v = K, \quad y = \frac{1}{\kappa^2 \operatorname{sn}^2 u}, \quad y - y_2 = \frac{\operatorname{dn}^2 u}{\kappa^2 \operatorname{sn}^2 u},$

$$\begin{aligned} \kappa(2H)t_2 &= \int \kappa^2 \operatorname{cn}^2 (K - u) du = \int_0^{\frac{1}{2}\pi} [\operatorname{dn}^2 (K - u) - \kappa'^2] du \\ &= \left( \frac{E}{K} - \kappa'^2 \right) u - \operatorname{zn} (K - u). \quad . . . . (4) \end{aligned}$$

19. In the Quadric Transformation (Q.T.) for the expression of  $x$  by the E.F. to modulus  $(\gamma, G)$ , in a sequence

$$\infty > a > b > x > c > d > -\infty,$$

as we have taken  $H$  positive and the orbit circling round the line  $SS'$ , in the expression

$$y = \frac{a-x}{b-x} \cdot \frac{x-d}{x-c}, \quad b, c = \pm 1, \quad . . . (1)$$

$$\frac{b-x}{a-x} = \frac{b-c}{a-c} \operatorname{sn}^2 \frac{1}{2} eG,$$

$$\frac{x-c}{a-x} = \frac{b-c}{a-b} \operatorname{cn}^2 \frac{1}{2} eG,$$

$$\frac{x-d}{a-x} = \frac{b-d}{a-b} \operatorname{dn}^2 \frac{1}{2} eG, \quad . . . . (2)$$

$$\gamma^2 = \frac{b-c}{a-c} \cdot \frac{a-d}{b-d}, \quad \gamma'^2 = \frac{a-b}{a-c} \cdot \frac{c-d}{b-d},$$

A.R.'s of  $a, b, c, d$ . And at  $x = \infty, y = 1,$

$$\gamma^2 \operatorname{sn}^2 \frac{1}{2} fG = \frac{b-c}{a-c}, \quad \operatorname{sn}^2 \frac{1}{2} fG = \frac{b-d}{a-d},$$

$$\operatorname{cn}^2 \frac{1}{2} fG = \frac{a-b}{a-d}, \quad \operatorname{dn}^2 \frac{1}{2} fG = \frac{a-b}{a-c}, \quad . . (3)$$

$$\frac{b-x}{a-x} = \gamma^2 \operatorname{sn}^2 \frac{1}{2} eG \operatorname{sn}^2 \frac{1}{2} fG,$$

$$\frac{x-c}{a-x} = \frac{\gamma^2 \operatorname{cn}^2 \frac{1}{2} eG \operatorname{sn}^2 \frac{1}{2} fG}{\operatorname{dn}^2 \frac{1}{2} fG},$$

$$\frac{x-d}{a-x} = \frac{\operatorname{dn}^2 \frac{1}{2} eG \operatorname{sn}^2 \frac{1}{2} fG}{\operatorname{cn}^2 \frac{1}{2} fG}, \quad . . . . (4)$$

$$\begin{aligned}
 y &= \frac{\operatorname{dn}^2 \frac{1}{2} e G}{\gamma^2 \operatorname{sn}^2 \frac{1}{2} e G \operatorname{cn}^2 \frac{1}{2} e G} \cdot \frac{\operatorname{dn}^2 \frac{1}{2} f G}{\gamma^2 \operatorname{sn}^2 \frac{1}{2} f G \operatorname{cn}^2 \frac{1}{2} f G} \\
 &= \frac{1 + \operatorname{dn} e G}{1 - \operatorname{dn} e G} \cdot \frac{1 + \operatorname{dn} f G}{1 - \operatorname{dn} f G} \\
 &= \frac{1}{\kappa^2 \operatorname{sn}^2 e K \operatorname{sn}^2 f K} = \frac{1}{\kappa^2 \operatorname{sn}^2 u \operatorname{sn}^2 v}, \quad (5)
 \end{aligned}$$

in accordance with the Q.T. in (1) above.

Other Q.T. formulas are

$$\sqrt{\kappa \operatorname{sn} e K} = \gamma \operatorname{sn} \frac{1}{2} e G \operatorname{sn} (1 - \frac{1}{2} e) G, \quad \dots \quad (6)$$

so that, when  $e=0$ ,

$$\begin{aligned}
 \sqrt{\kappa K} &= \frac{1}{2} \gamma G \quad \text{and} \quad \sqrt{\kappa K'} = \gamma G', \\
 \frac{K'}{K} &= \frac{2G'}{G}, \quad \kappa = \frac{1 - \gamma'}{1 + \gamma'}, \quad \dots \quad (7)
 \end{aligned}$$

$$\frac{1}{2} e G = \int_x^b \frac{\frac{1}{2} \sqrt{(a-c) \cdot (b-d)} dx}{\sqrt{(a-x) \cdot (b-x) \cdot (x-c) \cdot (x-d)}}, \quad \dots \quad (8)$$

$$e K, K = \int_{y, y_1}^{\infty} \frac{\sqrt{(y_1 - y_3)} dy}{\sqrt{(4 \cdot y - y_1 \cdot y - y_2 \cdot y - y_3)}}, \quad \dots \quad (9)$$

Then, also,

$$\begin{aligned}
 \frac{1 - \operatorname{cn} f G}{1 + \operatorname{cn} f G} &= \frac{\operatorname{sn}^2 \frac{1}{2} f G \operatorname{dn}^2 \frac{1}{2} f G}{\operatorname{cn}^2 \frac{1}{2} f G} = \frac{b-d}{a-c}, \quad \frac{1 - \operatorname{dn} f G}{1 + \operatorname{dn} f G} = \frac{b-c}{a-d}, \\
 \operatorname{cn} f G &= \frac{a-b-c+d}{a+b-c-d}, \quad \operatorname{dn} f G = \frac{a-b+c-d}{a+b-c-d}, \\
 \operatorname{sn} f G &= \frac{2\sqrt{(a-c) \cdot (b-d)}}{a+b-c-d}, \quad \gamma \operatorname{sn} f G = \frac{2\sqrt{(a-d) \cdot (b-c)}}{a+b-c-d}, \\
 \gamma' \operatorname{sn} f G &= \frac{2\sqrt{(a-b) \cdot (c-d)}}{a+b-c-d} \dots \dots \quad (10)
 \end{aligned}$$

A modification will be required with  $b, c$  conjugate imaginary, and  $a, d = \pm 1$ , with the sequence

$$\infty > x > a > d > x > -\infty,$$

and

$$y = \frac{x-b \cdot x-c}{x-a \cdot x-d} = \frac{(x-m)^2 + n^2}{x^2 - 1} = \frac{x^2 - \frac{A-B}{H} x - 1 - \frac{K}{H}}{x^2 - 1}.$$

Then with  $(a-m)^2 + n^2 = H^2$ ,  $(d-m)^2 + n^2 = K^2$ ,

$$\kappa^2 = \frac{(H+K)^2 - (a-d)^2}{4HK}, \quad \kappa'^2 = \frac{(a-d)^2 - (H-K)^2}{4HK}.$$

$$2eG, 2fG = \int_1^{x, \infty} \frac{\sqrt{(HK)} dx}{\sqrt{X}},$$

$$\frac{x-1}{x+1} = \frac{H}{K} \cdot \frac{1 - \operatorname{cn} 2eG}{1 + \operatorname{cn} 2eG} = \frac{1 + \operatorname{cn} 2f}{1 - \operatorname{cn} 2f} \cdot \frac{1 - \operatorname{cn} 2e}{1 + \operatorname{cn} 2e},$$

$$\begin{aligned} x &= \frac{1 - \operatorname{cn} 2e \operatorname{cn} 2f}{\operatorname{cn} 2e - \operatorname{cn} 2f} \\ &= \frac{1}{2} \frac{\operatorname{sn}(f+e) \operatorname{dn}(f-e)}{\operatorname{dn}(f+e) \operatorname{sn}(f-e)} + \frac{1}{2} \frac{\operatorname{dn}(f+e) \operatorname{sn}(f-e)}{\operatorname{sn}(f+e) \operatorname{dn}(f-e)} \\ &= \frac{1}{2} \frac{\operatorname{cn}(1-f-e)}{\operatorname{cn}(1-f+e)} + \frac{1}{2} \frac{\operatorname{cn}(1-f+e)}{\operatorname{cn}(1-f-e)}, \end{aligned}$$

$$y = 4HK \frac{\operatorname{dn}^2 2eG}{\operatorname{sn}^2 2eG} = \frac{\operatorname{cn}^2(1-2f)G}{\operatorname{cn}^2(1-2e)G},$$

$$2eG, 2fG = \int_{y, y_1}^{\infty} \frac{\sqrt{(y_1 - y_3)} dy}{\sqrt{(4 \cdot y - y_1 \cdot y - y_2 \cdot y - y_3)}},$$

with  $y_2 = 0$ , and there is no Quadric Transformation in

$$y - y_1 = (1 - y_1) \frac{(x - x_1)^2}{x^2 - 1}, \quad y - y_3 = (1 - y_3) \frac{(x - x_3)^2}{x^2 - 1},$$

$$\frac{dy}{dx} = \frac{2m(x - x_1)(x - x_3)}{(x^2 - 1)^2}, \quad \frac{(y_1 - y_3) dy}{y - y_1 \cdot y - y_3} = \frac{2(x_1 - x_3) dx}{x - x_1 \cdot x - x_3},$$

$$y_1 - y_3 = HK = m(x_1 - x_3).$$

20. For the time  $t_1$ , change the sign of B, and write  $x$  for  $\operatorname{ch} \phi$ ; a similar reduction will hold, but in a new sequence

$$\infty > x > a > b > c > d,$$

$$\infty > y_1 > y_2 > 1 > y > y_3 = 0.$$

And when H is negative, the form of  $t_2$  will serve for  $t_1$ , with a sequence

$$\infty > a > x > d > b > c.$$

A Pseudo-Elliptic Case may be attempted, by taking  $f=1, \frac{1}{2}, \frac{2}{3}, \frac{1}{3}, \dots$ ; and then the Theta functions can be replaced by algebraical expressions.

*Phil. Mag.* S. 6. Vol. 46. No. 273. Sept. 1923. 2 C

XXXIX. *Energy Relations in the High-Tension Magneto.* By  
ELWYN JONES, M.Sc., *University Research Student, University College of North Wales, Bangor* \*.

THE problem of determining the energy of the induced primary current in a high-tension magneto from the various constants of the machine and the speed of rotation is of importance not only in connexion with the practical design of magnetos, but also on the theoretical side, especially in view of the well-known fact that the "permanent" magnet, between the poles of which the armature rotates, undergoes periodic fluctuations in strength during the rotation. The magnetic properties of the steel magnet are thus brought into play, and the question arises whether the changes of energy of magnetization of the magnet contribute in any appreciable degree to the useful energy produced by the machine.

The experiments described in the present paper were made with the object of determining in a particular case the values of the more important terms which appear in the energy equation of a magneto.

### *The Energy Equation.*

This equation may be expressed as follows:—

Mechanical work done in rotating the armature from a certain zero position, in which the contact pieces of the interrupter are brought together, to any position  $\theta^\circ$  from zero

$$\begin{aligned}
 &= \text{increase of magnetic energy of the system} \\
 &+ \text{heat generated in the primary wire between} \\
 &\quad \text{zero and } \theta^\circ \\
 &+ \text{thermal effects in the iron and steel portions of} \\
 &\quad \text{the machine} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)
 \end{aligned}$$

The magnetic energy of the system includes the following parts:—

(1) The electrokinetic energy of the induced current in the primary coil, represented in the usual notation by the integral  $\frac{1}{8\pi} \int BH \, dv$ , taken throughout the whole of the system and the surrounding space.—This part includes the

\* Communicated by Prof. E. Taylor Jones.

energy,  $\frac{1}{2}Li^2$ , due to the self-inductance of the primary coil and the current  $i$  induced in it, and the mutual energy of the primary coil due to its presence in the field of the magnet. The electrokinetic energy may also be expressed in the form  $\frac{1}{2}iN$ , where  $N$  is the total flux through the windings of the primary coil. The electrokinetic energy is zero in the zero position, in which  $i=0$ .

It should be explained that we are not here concerned with the conversion of the energy of the primary current into the energy of the secondary circuit, which is the immediate source of the energy of the spark. The manner of conversion of the primary energy is essentially the same in the magneto as in the induction coil, and has been fully discussed by Professor Taylor Jones in his 'Theory of the Induction Coil'\*. Our present problem is limited to the estimation of the amount of energy in the primary circuit which is available for such conversion, and this energy is represented by the term  $\frac{1}{2}Li^2$ .

(2) The intrinsic energy of magnetization.—According to the theory of Larmor†, the energy of magnetization is equal to the integral  $\frac{1}{2}\int BIdv$  taken throughout the volume of the iron and steel portions of the system. It is believed that at least a part of the change of energy of magnetization is compensated by thermal effects occurring within the magnetic material, but it does not appear to have been definitely ascertained whether the whole of the energy of magnetization is to be accounted for in this way.

Although the measurements described in the present paper allow of a determination of the change of energy of magnetization, we shall not include it as a separate term in the equation, but rather assume that it is partly compensated by the thermal effects forming the third term on the right-hand side of equation (1).

(3) The mutual energy of the magnetized material and the field in which it is placed.—The change of this part of the energy includes the integral  $v\int_0^H IdH$  or approximately  $\frac{v}{4\pi}\int_0^H BdH$  for each portion of the magnetized material, which gives in a closed cycle the usual hysteresis loss. The change of mutual energy may be estimated from the magnetization curves of the iron and steel. In the case of the iron it is comparatively small, owing to the small value of  $H$  in

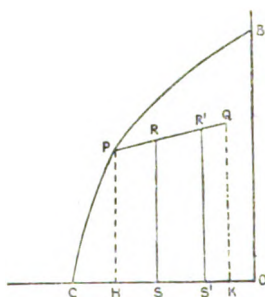
\* 'Theory of the Induction Coil' (Pitman & Sons, 1921).

† Proc. Roy. Soc. vol. lxxi. p. 229 (1902-3).

this material. In the case of the steel magnet, let BC in fig. 1 represent the "curve of demagnetization" of the magnet after its original magnetization, and let P, Q be the limits of the small cycle corresponding to any point P on the curve. The point P represents the greatest degree of demagnetization to which the magnet has been subjected. The point Q corresponds to the zero position of the armature.

Then the integral  $\int_0^\theta B dH$  for the magnet is represented approximately by the area RQKS, the point R corresponding to position  $\theta$ .

Fig. 1.



The change of mutual energy also includes a term  $r \int H dI$ , which we shall assume (as in the case of the energy of magnetization) to be in part compensated thermally.

The second term on the right-hand side of equation (1), the copper loss, is represented by the expression  $\int_0^\theta i^2 R \frac{d\theta}{\omega}$ , where  $R$  is the resistance of the primary wire and  $\omega$  is the speed of rotation.

In the third term on the right-hand side of (1), in addition to the thermal effects which are assumed to compensate the change of energy of magnetization, are also included losses due to eddy currents in the core and pole-pieces. Although the eddy current losses during the rapid oscillations which succeed the interruption of the primary current may be very considerable, it is not probable that they are serious in the comparatively slow changes of magnetization accompanying the rotation, more especially as the armature core is composed of thin insulated stalloy sheets.

With these modifications the energy equation becomes :

$$\text{Mechanical work } W = \frac{1}{2}Li^2 + \frac{1}{2}iN' + \frac{v_i}{4\pi} \int B_i dH_i + \frac{v_s}{4\pi} \int B_s dH_s + \int_0^\theta i^2 R \frac{d\theta}{\omega} + X_1, \quad (2)$$

where  $N'$  is the flux through the primary coil in the position  $\theta$  due to the magnet, and  $X_1$  represents any uncompensated magnetic energy of an intrinsic nature.

If the armature is rotated from 0 to  $\theta$  with the primary circuit open, the 1st, 2nd, and 5th terms on the right-hand side of (2) are zero, and the remaining terms are much smaller. The equation now becomes :

$$W' = \frac{v_i}{4\pi} \int_{i=0} B_i dH_i + \frac{v_s}{4\pi} \int_{i=0} B_s dH_s + X_2. \quad (3)$$

Subtracting (3) from (2), we find :

$$W - W' = \frac{1}{2}Li^2 + \frac{1}{2}iN' + \int i^2 R \frac{d\theta}{\omega} + \frac{v_s}{4\pi} [\text{area } RR'S'S] + \frac{v_i}{4\pi} \left[ \int B_i dH_i - \int_{i=0} B_i dH_i \right] + X, \quad (4)$$

$X$  being written for  $X_1 - X_2$ .

In a recent paper E. A. Watson \* has advanced theoretical reasons for the view that the quantity  $\frac{v_s}{4\pi} \int B_s dH_s$  representing the diminution of energy of the steel magnet is equal to the energy  $\frac{1}{2}Li^2$  in the armature coil available for conversion. In one case at any rate, viz. when the armature is rotated through  $180^\circ$  from zero, it might be expected that some relation must exist between the induced primary current and the demagnetization, since the demagnetization is in this case entirely due to the induced current. It is unlikely, however, that any such simple relation can exist in general: in some positions of the armature, for instance, the effect of the induced current is to increase rather than diminish the degree of magnetization of the magnet.

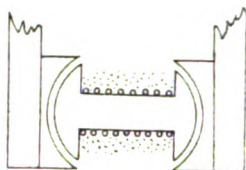
The experiments described below were arranged for the measurement of the terms in equation (4) for a certain speed of rotation. The measurements were made on a Thomson-Bennett Type A:D. 4 magneto.

\* Journ. Inst. Elect. Eng. vol. lix. no. 301 (May 1921).



In the present paper we shall take as the zero position of the armature that in which the axis of its coils is parallel to the field due to the magnet, as shown in fig. 2. The induced current therefore begins to grow from zero in this position.

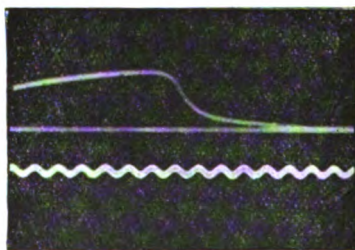
Fig. 2.



1. *Measurement of the induced current in any position of the armature.*

The induced current was determined by means of a current oscillograph designed by Professor Taylor Jones. By using an extra interrupter directly coupled with the armature and rotating with it, this instrument was connected in series with the primary coil. The photograph in fig. 3

Fig. 3.

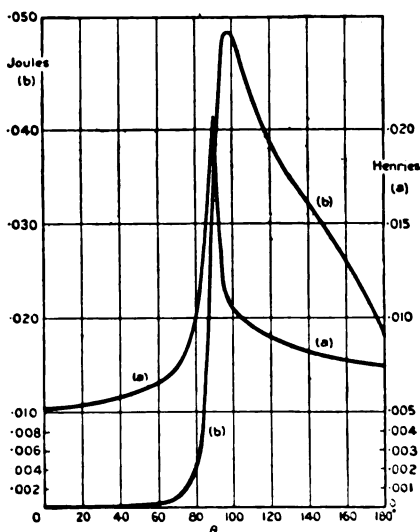


shows a typical curve obtained when the interrupter was so adjusted that contact was made when the armature was in the position shown in fig. 2, and broken when the armature was displaced through  $180^\circ$  from this position. The lower curve is the trace of a ray reflected from a 768 tuning-fork placed near the oscillograph. The curve in fig. 3 gives the value of the induced current at any position of the armature between  $0^\circ$  and  $180^\circ$ . The curve selected for measurement was taken when the armature was rotating at 1505 revolutions per minute. The maximum current at this speed was 3.12 amperes, and it occurred in the position of  $102^\circ$  from zero. The ordinate of the curve was measured in any position required (*i. e.* at any value of  $\theta$ ) by means of a travelling microscope.

## 2. Measurement of the primary self-inductance.

The current oscillograph was also used to determine the primary self-inductance in any position of the armature. The primary coil was connected in series with the oscillograph, and an A.C. voltmeter in parallel with both. The armature was locked in a position  $\theta^\circ$  and an alternating current, the R.M.S. value of which was the same as the induced primary current in that position, and whose frequency was approximately that of the rotating armature, was sent through the circuit. The curves obtained with the oscillograph gave the current wave-form, from which the R.M.S. value,  $i_s$ , was obtained in the usual way by dividing the maximum value by  $\sqrt{2}$ . The voltmeter (an instrument of the electro-dynamometer type) gave the R.M.S. voltage,  $V_s$ ,

Fig. 4.



at the terminals of the primary coil and oscillograph. The photographs also gave the frequency of the alternations of the current. The self-inductance was calculated from the relation  $V_s = i_s \sqrt{R^2 + 4\pi^2 n^2 L^2}$ , in which  $R$  represents the resistance of the primary coil and that of the oscillograph. The curve giving the self-inductance of the primary coil in different positions of the armature is shown in fig. 4 (a).

Owing to the low frequency at which the self-inductance was measured, the correction due to the presence of the secondary coil was found to be negligible.

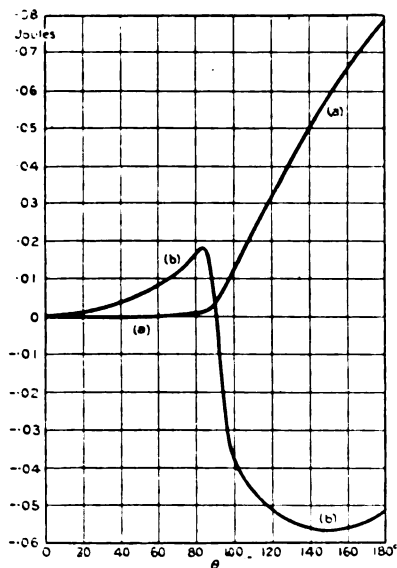
The available energy ( $\frac{1}{2}Li^2$ ) in any position  $\theta^\circ$  was obtained from the foregoing results, and its variation with  $\theta$  is shown in fig. 4 (b).

### 3. *Determination of the heat loss in the primary wire.*

The heat generated in the primary circuit between zero and  $\theta^\circ$  was obtained from the area of the  $i^2R$  curve between zero and  $\theta^\circ$ . The resistance  $R$ , being the total resistance of the circuit traversed by the current  $i$ , included the resistance of the oscillograph and connecting wires. The curve (a)

in fig. 5 gives the value of the copper loss,  $\int i^2 R \frac{d\theta}{\omega}$ , in different positions of the armature.

Fig. 5.



### 4. *Measurement of the change of induction in the magnet.*

A number of small coils were wound on the magnet in different places, and the change of flux through these coils due to rotating the armature from zero to  $\theta^\circ$  was measured by connecting them in turn to a ballistic galvanometer. The contact pieces of the interrupter were kept apart during the rotation. Dividing these flux changes by the area of cross-section of the magnet and taking the mean, we find the

change of magnetic induction in the magnet due to rotating the armature.

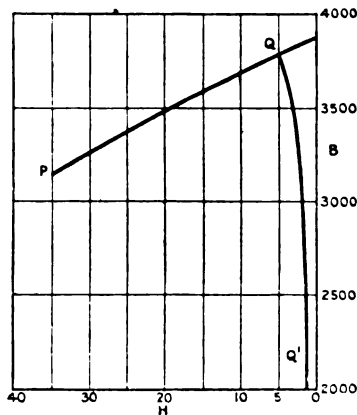
The armature was then clamped in the position  $\theta^\circ$ , and the current corresponding to that position was sent through the primary coil, one of the magnet coils being connected to the galvanometer. The change of flux in the magnet due to switching on this current in the armature was measured as before.

Combining the two results, we have the total change of magnetic induction in the magnet for the position  $\theta^\circ$  of the armature. It was found that the maximum demagnetization of the magnet occurred at  $125^\circ$ .

### 5. *Determination of the BH curve for the magnet.*

The primary coil was connected to a ballistic galvanometer, and the change of flux through the coil due to rotating the armature from zero to  $180^\circ$  was determined. This gave twice the actual flux passing through the armature in the zero position. Dividing the latter by the area of cross-section of the magnet and adding a correcting term due to

Fig. 6.



leakage flux, we obtain the ordinate of the point Q in figs. 1 and 6. The leakage-flux was obtained by means of an exploring coil, connected to a ballistic galvanometer and placed above and below the armature. The abscissa of the point Q was obtained from the relation

$$H_Q = \frac{N}{L} \left( \frac{2d}{A} + \frac{l}{\mu s} \right),$$

which represents the fact that the magnetomotive force in

the armature and air-gaps is equal to the M.M.F. demagnetizing the magnet\*. In this equation

$N$  = flux through the armature in the zero position,

$L$  = length of the steel magnet,

$d$  = thickness of the air-gap between the armature and pole-shoes,

$A$  = area of the curved end of the armature core,

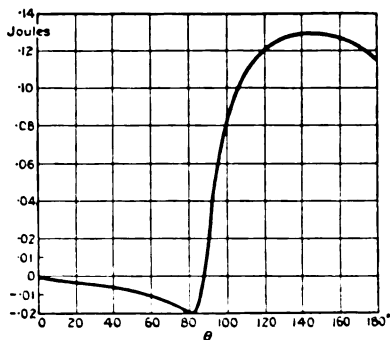
$s$  = area of cross-section of the armature core,

$\mu$  = permeability of stalloy corresponding to a flux density  $\frac{N}{s}$ ,

$l$  = length of the armature core along the axis.

The point Q in fig. 6 lies upon the magnetization curve for the armature and air-gaps represented by QQ', various points on which were determined in the same way for other values of the flux density. The magnet was subjected to a demagnetizing force by means of a current passing through a coil wound over the whole length of the magnet, the change of induction in the magnet being measured as before. The demagnetizing force was varied by varying the current, and was gradually increased until the magnetic induction reached the minimum obtained in the experiments described in the previous section. The demagnetization curve obtained for the magnet is the line QP in fig. 6.

Fig. 7.



From these and the results of the measurements described in section 4, the term  $\frac{r_s}{4\pi}$  [area RR'S'S] (fig. 1) in equation (4) was calculated for different values of  $\theta$ , and the curve is shown in fig. 7.

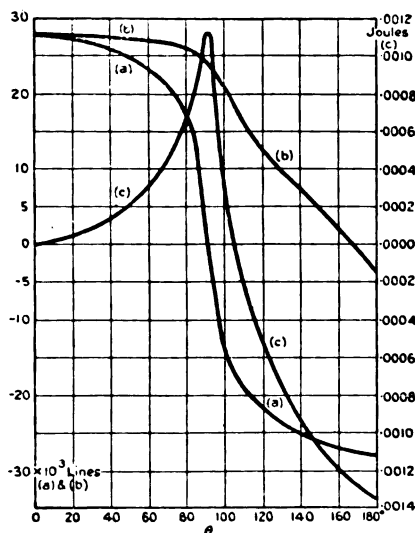
\* The magnetic reluctance of the wide cheeks of the armature and of the pole-pieces is neglected.

# 6. Measurement of the mutual energy of the iron and the field.

The flux due to the magnet through the armature in the position  $\theta^\circ$  was obtained by connecting the primary coil to a ballistic galvanometer and determining the change of flux produced by rotating the armature from zero to  $\theta^\circ$ . Subtracting this from the original flux passing through the armature in the zero position, we find the flux in position  $\theta^\circ$ . The open-circuit flux wave is shown in fig. 8 (a). This value for the flux has to be divided by the area of cross-section of the armature core, in order to reduce it to flux density in the iron.

The flux through the armature due to the current in the position  $\theta^\circ$  was obtained by locking the armature in this

Fig. 8.



position, connecting the secondary to a ballistic galvanometer and sending the current corresponding to this position through the primary coil. A correction had to be applied to the flux thus obtained, owing to the change in the magnet flux through the armature due to the demagnetizing effect of the current on the magnet. The amount of demagnetization of the magnet due to the current in the position  $\theta^\circ$  had been determined in a previous experiment (see section 4, above).

Fig. 8 (b) shows the total flux through the armature in any position during one half-revolution.

Reducing these to flux densities in the armature core and from measurements of the areas in the BH curve for a typical specimen of silicon steel, the term

$$\frac{r_i}{4\pi} \left[ \int B_i dH_i - \int_{i=0} B_i dH_i \right]$$

was calculated for different values of  $\theta$ , and is shown in fig. 8 (c). Since this term is small in comparison with the other terms of equation (4), it was thought sufficient to obtain its value from a typical specimen of silicon steel instead of determining the BH curve for the actual material of the core.

7. The term  $\frac{1}{2}iN'$  was obtained from the open-circuit flux wave, a correction being applied due to the reduction of the magnet flux through the armature caused by the induced current. The manner in which this correction was obtained is described in section 6. The values of the term  $\frac{1}{2}iN'$  are shown in fig. 5 (b).

#### 8. *Measurement of the work done.*

The couple acting on the armature in the position  $\theta^\circ$  was measured when the current corresponding to that position was flowing through the primary wire. For this purpose a lever was attached to one end of the armature axle, and a cord, passing from one end of the lever and over a pulley, supported a scale-pan. The position of the pulley was so adjusted that in each position of the armature the cord was at right angles to the lever. In this way the couple was measured which was necessary to hold the armature in the position  $\theta^\circ$  with the appropriate current flowing in its primary coil. This experiment was then repeated with the primary circuit open, and in this case the couple measured is that required to hold the iron core in the position  $\theta^\circ$ .

These couples were plotted against  $\theta$ , and the area of the curve from zero to  $\theta^\circ$  gives the work done,  $W$  or  $W'$ .

The difference  $W - W'$  is shown in fig. 9 (a)\*.

The results of all the above measurements are collected in the Table, in which the first column gives the position  $\theta^\circ$  of the armature, the second column the work done  $W$  in turning the armature from 0 to  $\theta$  in joules, the third the work done  $W'$  on open circuit, the fourth the values of the useful energy  $\frac{1}{2}Li^2$ , the fifth the mutual energy  $\frac{1}{2}iN'$  of the primary

\* Frictional work is neglected, being practically eliminated by the process of taking the difference between  $W$  and  $W'$ : its value is in any case small.

TABLE.

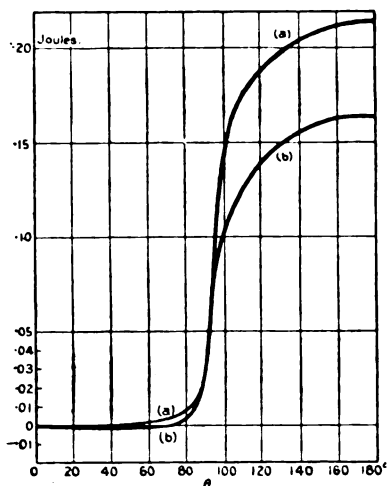
(1) $\theta$ .	(2) W.	(3) W.	(4) $\frac{1}{2}Lr^2$ .	(5) $\frac{1}{2}N'$ .	(6) $\int_{-\omega}^{\theta} r^2 R \frac{d\theta}{\omega}$ .	(7) $\frac{v}{4\pi} \int B_r d\Pi_r$ .	(8) $\frac{v}{4\pi} \int B_r d\Pi_r$ .	(9) $\Sigma$ .	(10) W-W'.
0	0	0	0	0	0	0	0	0	0
20	-00128	-00118	-000018	-00207	-00001	-00314	-00004	-00108	-000103
40	-00436	-00453	-000114	00484	-000039	-00625	-00012	-00137	-000429
60	-0117	-00996	-000498	-00860	-000233	-0105	-00033	-00152	-00176
70	-0171	-0137	-00121	-0117	-000471	-0135	-000436	-00055	-00338
80	-0271	-0190	-00461	-0164	-00112	-0180	-00065	-00345	-00813
85	-0376	-0229	-0141	-0171	-00185	-0188	-00081	-00135	-0148
90	-0643	-0241	-0350	-00294	-00369	-00258	-0011	-0405	-0402
95	-120	-0255	-0500	-0190	-00758	-0454	-00787	-0831	-0949
100	-168	-0224	-0409	-0376	-0127	-0806	-000354	-105	-146
110	-193	-0175	-0438	-0465	-0230	-106	-000235	-127	-175
120	-204	-0141	-0384	-0510	-0326	-120	-000507	-140	-190
140	-215	-00900	-0318	-0560	-0502	-129	-000970	-156	-206
160	-219	-00607	-0256	-0559	-0659	-128	-00117	-164	-213
180	-220	-00507	-0180	-0512	-0784	-116	-00136	-163	-215



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coil at  $\theta^\circ$ , the sixth the copper loss during the rotation 0 to  $\theta^\circ$ , the seventh and eighth the loss of mutual energy of the magnet and of the iron core. The ninth column gives the sum of the terms in columns (4) to (8). The last column shows the value of the mechanical work  $W - W'$  in the various positions of the armature. The values given in the last two columns are also shown graphically in fig. 9, in which curve (a) represents the mechanical work  $W - W'$ , and (b) the values given in column (9)—i. e., the total change of magnetic energy (excluding unbalanced intrinsic effects) and the heat loss in the primary wire.

Fig. 9.



It will be seen from fig. 9 that in the neighbourhood of the position  $90^\circ$  the two curves agree closely; at smaller values of  $\theta$ ,  $W - W'$  slightly exceeds the magnetic and thermal effects represented in column (9); at larger angles the difference increases, and at  $180^\circ$  about 25 per cent. of the mechanical work done in rotating the armature is unaccounted for by the quantities represented in Table I.

The conclusion to which these experiments point is that the energy developed in the primary coil by its rotation in the field of the magnet is at and near the  $90^\circ$  position (which is the position at which the secondary spark is usually obtained) entirely accounted for by the mechanical, magnetic, and thermal energy in the manner explained above. For positions representing larger angles of rotation of the armature ( $100^\circ$  to  $180^\circ$ ) there appears to be a loss of energy

from the forms considered in this paper. Possibly this difference appears as heat in the iron and steel of the machine.

With regard to Watson's conclusion that the loss of magnetic energy of the magnet (column (7), Table) is equal to the useful electrokinetic energy generated in the primary coil, together with the heat loss in the primary wire (columns (4) and (6), Table), it will be seen that, according to the measurements described in the present paper, at  $180^\circ$  the loss of energy of the magnet is about 20 per cent. greater than the sum of the electrokinetic energy and the copper loss. The difference is much greater at  $120^\circ$ , and sinks to zero at  $97^\circ$ . At still smaller angles the magnet term is much smaller than the sum of the electrokinetic energy and the copper loss, and is in fact negative at angles less than  $90^\circ$ .

It does not appear therefore that there is any simple relation between the loss of energy of the magnet, as represented by the area  $RR'S'S$  in fig. 1, and the useful electrokinetic energy generated in the primary coil.

The efficiency with which useful energy is developed is represented by the ratio of the numbers in the fourth and second columns. The efficiency has a maximum value of about 54 per cent. at  $90^\circ$ .

The experiments described above were carried out in the Physical Laboratories of the University College of North Wales, Bangor. In conclusion, I wish to thank Professor E. Taylor Jones for his most valuable assistance in everything connected with this paper.

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*XL. Linear, Exponential, and Combined Dampings exhibited by Pendulum Vibrations.* By Prof. E. H. BARTON, F.R.S., and H. M. BROWNING, M.Sc., Ph.D., University College, Nottingham\*.

[Plates VI. & VII.]

IT is well known that under resistances proportional to the speed, a vibration is exponentially damped. It is consequently never extinguished. Yet we are not aware that all vibrations once started are still in operation. It would therefore appear that vibrations, whether mechanical or electrical, are really subject to other resistances than that single type proportional to the speed which is conventionally

\* Communicated by the Authors.

postulated. In July 1922\* H. S. Rowell considered theoretically the case of a vibration under a constant resistance, and showed that it resulted in linear damping.

It seemed of interest to the present writers to obtain experimental illustrations of such vibrations in the simplest mechanical manner. This has now been done for vibrations with linear dampings only, exponential only, and for a combination of both. The theory developed for these cases is in satisfactory agreement with the experiments. The vibration records consist of photographs of salt traces left by a pendulum. The damping of this pendulum was produced by (1) solid friction on its lath, or by (2) fluid friction due to air resistance increased by a card, or by (3) both together.

#### THEORY.

*General Equation for Combined Damping.*—We may write the equation of motion for combined damping as follows:—

$$m \frac{d^2 y}{dt^2} + r \frac{dy}{dt} + sy \pm F = 0, \quad . . . . (1)$$

$$\text{or} \quad \frac{d^2 y}{dt^2} + 2k \frac{dy}{dt} + p^2(y \pm S) = 0, \quad . . . . (2)$$

where  $y$  is the displacement and  $m$  is the mass of the vibrating particle,  $s$  is the restoring force per unit displacement,  $r$  is the fluid resistance per unit speed,  $F$  is the solid resistance of constant numerical value, but of sign opposite to that of the velocity; also

$$2k = \frac{r}{m}, \quad p^2 = \frac{s}{m}, \quad S = \frac{F}{s}. \quad . . . . (3)$$

Thus (1) and (2) only hold, with a certain sign of  $F$ , for a single half period from one maximum elongation to the next of opposite sign.

Consider first the half period from rest at a positive elongation. Then we may write for this *start* of the motion,

$$\text{for} \quad t = 0, \quad \frac{dy}{dt} = 0, \quad y = S + A. \quad . . . . (4)$$

Then the solution of (1) and (2) for the half period defined by (4) requires the negative sign for  $F$  and  $S$ , and may be written:

$$y - S = Ae^{-kt} \left( \cos qt + \frac{k}{q} \sin qt \right), \quad . . . . (5)$$

where

$$q^2 = p^2 - k^2. \quad . . . . . (6)$$

\* See Phil. Mag. xliv. pp. 284-285.

It will be seen that this solution satisfies the conditions expressed in equations (4).

The negative elongation  $y_1$ , at the end of this first half period, is found by putting in (5)  $t = \pi/q$ . We thus obtain

$$y_1 - S = -Ae^{-k\pi/q} = -A\rho, \quad \dots \quad (7)$$

where

$$\rho = e^{-k\pi/q}. \quad \dots \quad (8)$$

For the second half period  $F$  and  $S$  change sign so that the axis of our exponentially damped vibration is  $-S$ . And the initial state for this second half period is that given at the end of the first. So for the second half period, if we again let  $t$  start from zero, the solution may be written

$$y + S = -(A\rho - 2S)e^{-kt} \left( \cos qt + \frac{k}{q} \sin qt \right). \quad \dots \quad (9)$$

Proceeding thus we find at the end of the second half period the elongation  $y_2$  given by

$$y_2 + S = (A\rho - 2S)\rho = A\rho^2 - 2S\rho. \quad \dots \quad (10)$$

And by continuing in this way we find that after  $n$  half periods the original amplitude of  $S + A$  becomes reduced to  $y_n$  where

$$y_n \pm S = \pm A\rho^n \mp 2S(\rho^{n-1} + \rho^{n-2} + \dots + \rho), \quad \dots \quad (11)$$

the upper signs being used for  $n$  even and the lower signs for  $n$  odd.

To make comparisons of recorded dampings which are (1) exponential only, (2) linear only, and (3) a combination of the two, we need some simple way of gauging the damping in each case. It seems desirable for this purpose to fix upon the number of half periods in which the elongation is reduced to one-half. The half is chosen rather than zero because in the latter case for purely exponential damping the number would be infinite.

Thus, if in  $n$  half periods the original elongation ( $S + A$ ) becomes reduced to one-half by combined damping, we have, from (11),

$$\begin{aligned} y_n &= \mp S \pm A\rho^n \mp 2S(\rho^{n-1} + \rho^{n-2} + \dots + \rho) \\ &= \frac{S + A}{2}, \end{aligned}$$

$$\text{or} \quad n = \log \left\{ \frac{A(1-\rho) + S(3+\rho)}{2A(1-\rho) + 4S} \right\} \div \log \rho. \quad \dots \quad (12)$$

*Linear Damping.*—For  $k=0$  in (2) the exponential damping disappears, and the result is a linear damping. In other words, the elongations form an arithmetical progression whose common difference is  $-2S$ , as seen from equations (4), (7), (10), and (11) for  $\rho=1$ . Hence, if in  $a$  half periods the original elongation  $S+A$  is halved, we have

$$S+A-(2S)a = \frac{S+A}{2},$$

whence 
$$S = \frac{A}{4a-1} \quad \text{and} \quad a = \frac{S+A}{4S} \quad \dots \quad (13)$$

*Exponential Damping.*—For  $F=0$  in (1) we have  $S=0$  in (2) and the subsequent equations; thus the damping is exponential only, or the successive elongations are in geometric progression. Hence, if in  $b$  half periods the original amplitude  $(S+A)$  is halved, we have

$$e^{-k\pi b/q} = 1/2. \quad \dots \quad (14)$$

*Comparison of Pure and Combined Dampings.*—By equations (8) and (14) we see that

$$\rho^b = 1/2 \quad \text{or} \quad \rho = 2^{-1/b}. \quad \dots \quad (15)$$

Therefore, putting (13) in (12), we find

$$n = \log \frac{2a(1-\rho) + (1+\rho)}{4a(1-\rho) + (1+\rho)} \div \log \rho, \quad \dots \quad (16)$$

which gives  $n$  in terms of  $a$  and  $\rho$ ; and since, as shown in (15),  $\rho$  is the  $b$ th root of one-half, this may be regarded as giving  $n$  in terms of  $a$  and  $b$ .

*Approximation.*—When  $\rho$  is nearly unity, we may write  $(1+\rho)=2$  and  $(1-\rho)=\sigma$ ; then (16) becomes

$$n = \log \frac{1+a\sigma}{1+2a\sigma} \div \log \rho = \left[ \log \frac{1+a\sigma}{1+2a\sigma} \right] \div (-\sigma). \quad (17)$$

*Experimental Arrangements.*—As shown in the photograph of the apparatus (Pl. VI.), the pendulum suspension was a wood lath. On this a card could be attached to increase the fluid friction, and also rubbers made by means of an inverted clip stand could be pressed upon the upper part of the lath to introduce the solid friction. The bob was usually a ring of iron containing a funnel of Cerebos Salt to leave a vibration trace on the board which ran on rails and was drawn along by hand, constancy of speed being assured by the aid

of a metronome. This method was readily adaptable to any desired conditions, and seemed preferable to the use of a motor.

*Results.*—About fifty photographs of traces were taken, of which twenty-five are reproduced on Pl. VII., and the conditions under which they were obtained are summarized as follows:—

*Conditions under which Vibrations occurred.*

No. of Figure.	RUBBER.	CARD.	BOB.
1 .....	Wash-leather.....	None .....	Iron.
2 .....			
3 .....			
4 .....			
5 .....			
6 .....	Cork and Graphite...	None .....	Iron.
7 .....			
8 .....			
9 .....			
10 .....			
11 .....	Cork, Graphite, and Vaseline .....	None .....	Iron.
12 .....			
13 .....			
14 .....			
15 .....			
16 .....	No rubber .....	Card 10 inches by 5 inches .....	{ No Iron, but only glass fun- nel supported by wire, to con- tain Salt.
17 .....	Rubber of Cork, Graphite, and Vaseline.....		
18 .....			
19 .....			
20 .....			
21 .....	Cork, Graphite, and Vaseline .....	Card 10 in. × 5 in.	} Iron.
22 .....		„ 16 in. × 14 in.	
23 .....		„ 16 in. × 14 in.	
24 .....		None .....	
25 .....	No rubber .....	Card 16 in. × 14 in.	

The records fall into five sets of five each, and throughout each of the first four sets the damping increases as we proceed in that set. In the last set, which is very special, this is not so.

In the first set (figs. 1-5)\* the rubbers were of wash-leather, and evidently for light pressures these did not, on reversal, give the discontinuity of force characteristic of solid friction. This is seen by the damping which at first (fig. 1) approaches exponential and is finally (fig. 5) almost linear.

\* The references in the text are to the *Arabic* numerals on the figures. The Roman numerals indicate simply the order of taking the records.

The second set (figs. 6-10), with cork rubbers lubricated with fine graphite powder (as used in the carriages of lace machines), show for the higher pressures the linear dampings characteristic of solid friction. Probably for the very light pressures the contact was not quite continuous, and therefore the damping was not pure.

The third set (figs. 11-15), with vaseline added on the rubbers, seemed to ensure continuous contact, and gave throughout dampings almost linear.

The limits  $y = \pm S$  are experimentally shown on figs. 9, 13, and 15. These were obtained by giving the pendulum the maximum displacement which failed to elicit any return motion, since the restoring force was balanced by the opposing frictional force. Figs. 10 and 14 have the centre line,  $y=0$ , shown.

It is to be noticed that when first a state of rest is reached anywhere between the limits  $y = \pm S$ , then the vibration ceases, as may be noticed in the above-mentioned figures. The quick-period quivers shown on figs. 9, 10, 13, 14, and 15 are due to a slight flexibility of the lath not contemplated in the theory.

Figs. 13 and 15 give interesting confirmations of theory as to the relation of the damping to these limits. For from equation (13) we may write

$$\text{Number of half periods to extinction} = \frac{\text{Initial Amplitude}}{\text{Distance between limits}}.$$

In the two cases under notice we have

$$\frac{2.7}{0.35} = 7\frac{1}{2}, \text{ or, say, 8 half periods,}$$

$$\frac{2.7}{0.9} = 3 \text{ half periods.}$$

The fourth set (figs. 16-20) consists of vibrations of the pendulum without any iron in the bob, but only the glass funnel and salt. A card 10 inches by 5 inches was fastened at the bottom of the lath to effect by air resistance considerable damping of this light pendulum. For fig. 16 no rubbers were in use, and the damping due to fluid friction is seen to be sensibly exponential. For figs. 17-20 the rubbers were used, and with successively greater pressures. The dampings are seen to approach linearity as the solid friction becomes paramount. Fig. 20 has the limits  $y = \pm S$  shown, and therefore reveals the effect of the card in contrast with figs. 13 and 15, for which no card was in use,

In the fifth set (figs. 21-25) the iron bob was restored and used throughout. In figs. 21 and 22 the cards in use were 10 in. by 5 in. and 16 in. by 14 in. respectively, rubbers being in use as well. Thus both are examples of combined damping, but fig. 22, with the larger card and therefore more fluid friction, shows greater departure from the linearity characteristic of the damping due to solid friction. It is, however, noticeable that with both practical extinction obtains. This is in marked contrast to cases of purely exponential damping, which are alone dealt with in traditional theory.

Figs. 23-25 give the data for tests of the theory already developed (1) on combined damping and its relation to the components, and (2) on some characteristics of those components when occurring alone. Really four photographs were taken, beginning with a plate, not shown, in which the pendulum had the rubbers in a certain adjustment but with no card on the lath. The result was indistinguishable from the third one with rubbers and no card, and here given as fig. 24. Between these a record was taken with the card 16 in. by 14 in. attached to the lath, but with no change of rubbers. The result of this is shown in fig. 23. The agreement of fig. 24 with the record not shown gave the required assurance that the rubbers had not by any chance become altered by the attachment and removal of the card. Finally, fig. 25 was obtained by the removal of the rubbers, the card remaining attached to the lath.

Thus, applying to figs. 23, 24, and 25 the results given in equations (12)-(15), we have

$$\left. \begin{array}{l} a = 8.5, \\ b = 14, \end{array} \right\} \text{by inspection of records,}$$
$$n = 5.2, \quad \text{by theory,}$$

or  $n = 5$  nearly, by inspection.

These form a fair agreement.

In fig. 24 we have two sets of vibrations with different initial amplitudes, but obtained under precisely the same conditions, the damping being linear. These serve to illustrate equation (13), which shows that the number of periods for reduction of amplitude to half value depends upon the initial amplitude as well as upon the damping in use.

In contrast to this we have in fig. 25 two sets of vibrations with different initial amplitudes, but under the same conditions, the damping being purely exponential. Here it can be seen that the number of periods required for reduction to



half amplitude is independent of the initial amplitude, and depends solely upon the damping in use according to the well-known expression (see equation (5)).

*Conclusion.*—It would seem from the remarks of Mr. H. S. Rowell (Phil. Mag. xliv. p. 951, Nov. 1922), and in the light of the above experiments, that vibrational methods might prove useful in the investigation of the type of resisting force introduced by various lubricants.

Also it may be noted that in the case of many electrical vibrations it is quite possible that spark gaps or other phenomena play the part of solid friction in mechanical vibrations, and so ensure the extinction of these electrical vibrations. But hitherto the cause of any such resistance in the electrical case does not appear to have received the attention it deserves.

Nottingham,  
May 3rd, 1923.

## XLI. *On Sub-Continental Temperatures.*

*By H. H. POOLE, Sc.D.\**

### *Introduction.*

THE theory of radioactive revolutions, recently put forward by Dr. Joly, is based on the apparently justifiable assumption that the radioactivity of the basaltic magma, on which the continental rocks are thought to float, is approximately the same as that of basalt extruded at the surface. It seems to be natural to make the same assumption with regard to the continental rocks. This, however, is contrary to the view previously held that the smallness of the temperature gradient underground involved a very definite limit to the extent in depth of rocks of the relatively high radioactivity met with at the surface †. It may be of interest to reconsider this question, in order to ascertain whether the assumption of uniform radioactivity to the bottom of the continental crust would really involve any serious discrepancy with known facts.

\* Communicated by the Author.

† Joly, Phil. Mag. October 1912, p. 701. The present paper was almost completed when Joly's most recent paper (Phil. Mag. June 1923) appeared.

*Distribution of Temperature in a Uniform Layer.*

Let us in the first place assume that throughout a layer of the crust, of thickness  $h$ , the thermal conductivity,  $K$ , and the rate of generation of heat per unit volume,  $q$ , are both constant. Let us further assume that, as the continental rocks are not considered to undergo extensive fusion during periods of revolution, the loss of heat from them during these periods is not greatly above the average, so that their temperatures during normal periods are approximately constant, the surface being at a temperature  $\theta_1$  and the base of the layer at a temperature  $\theta_2$ , which, as will be seen later, should probably be about the melting-point of basalt.

It is easily seen, then, that the temperature,  $\theta$ , at a depth  $x$  is given by the equation

$$\theta = \theta_1 + ax - \frac{qx^2}{2K},$$

where  $a$ , the temperature gradient just below the surface, equals

$$\frac{\theta_2 - \theta_1}{h} + \frac{qh}{2K}.$$

It is evident that  $a$  would be a minimum if

$$h = \sqrt{\frac{2K(\theta_2 - \theta_1)}{q}}.$$

If the thickness of the layer exceeds this value, a maximum temperature,  $\theta_1 + \frac{Ka^2}{2q}$ , will occur at a depth  $\frac{Ka}{q}$ , i. e.

$$\frac{K(\theta_2 - \theta_1)}{qh} + \frac{h}{2}.$$

Below this the flow of heat must take place in a downward direction. What would actually become of this heat is considered later.

If we assume that the average continental rocks are of an "intermediate" character\*, we may take as their average Radium content  $2 \times 10^{-12}$  g. per g. †, and as their Thorium content  $1.5 \times 10^{-5}$  g. per g. ‡. Taking the rock density to be 2.7, we find  $q = 6.4 \times 10^{-13}$  calory per second per c.c. If we assume that  $K = 4 \times 10^{-3}$  c.g.s. units,  $\theta_1 = 15^\circ$  C., and

\* Clarke, 'Data of Geochemistry,' 2nd Edition, p. 26 (1911).

† Joly, *loc. cit.*

‡ J. H. J. Poole, Phil. Mag. April 1915, p. 489.

$\theta_2 = 1215^\circ \text{C.}$ , we find that  $a$  has the minimum value  $6.2 \times 10^{-4}$  degree per centimetre if  $h = 38.7$  kilometres. The thickness to be ascribed to the continental mass varies with the height of the land, and also with the level assumed for the upper surface of the basaltic magma in the oceanic areas. The values of  $a$  and the maximum temperature  $\theta_m$  for various values of  $h$  are as follows :—

$h \dots$	20	30	40	50	60	70	80	90	100 kilometres.
$a \dots$	7.6	6.4	6.2	6.4	6.8	7.3	7.9	8.5	$9.2 \times 10^{-4}$ degrees per cm.
$\theta_m \dots$	—	—	$1215^\circ$	$1295^\circ$	$1460^\circ$	$1680^\circ$	$1960^\circ$	$2270^\circ$	$2660^\circ \text{C.}$

It is obvious that for the thicker layers, fusion of the acid rocks might be expected to occur. It is possible that these conditions might be realized at the bases of mountain chains, especially during mountain-building epochs.

*Discrepancy between the Estimated and the Actual Temperature Gradients.*

We see that the temperature gradient just below the surface to be expected on these hypotheses is at least  $6 \times 10^{-4}$  degrees per cm., whereas the actual gradient only averages about  $3 \times 10^{-4}$ . The discrepancy at first sight appears to be rather serious, but there would seem to be several causes tending to reduce the gradient in the neighbourhood of the surface, where alone it is capable of measurement.

*Effect of Temperature on the Thermal Conductivity of Rocks.*

We have assumed above that  $K$  is constant and has the value  $4 \times 10^{-3}$ . Now Debye has shown that we should theoretically expect the conductivity of a crystal to vary inversely as its absolute temperature; and this has been experimentally verified by Eucken\*, who found also that the conductivity of crystalline substances, such as marble, fell with rise of temperature, though not so rapidly as that of pure crystals, while the conductivity of amorphous bodies rose with rise of temperature. This is in complete agreement with some determinations by the writer on the thermal conductivities of rocks, although the results in this case were complicated by permanent changes†. It was found that the conductivity of a typical specimen of granite fell from  $5.7 \times 10^{-3}$  at  $105^\circ \text{C.}$  to  $3.8 \times 10^{-3}$  at  $516^\circ \text{C.}$  A considerable part of this fall was of a permanent nature and was attributed to minute cracking,

\* *Ann. der Phys.* xxxiv. p. 185 (1911).

† *Phil. Mag.* July 1912 and January 1914.

but there was also evidence of a considerable recovery of conductivity when the temperature was again reduced. Results of a similar nature were obtained with limestone. Basalt, on the other hand, which was largely glassy, had a conductivity close to  $4 \times 10^{-3}$  almost independent of temperature up to  $600^{\circ}\text{C}$ .

We thus see that there is considerable reason, both theoretical and experimental, for assuming a fall in conductivity with rise in temperature in crystalline rocks. If the writer's figures may be taken as a guide, we would not be very far from the truth in taking  $K = 6 \times 10^{-3}$  for granite and limestone close to the surface. No results were obtained for slate, owing to splitting of the rock. A mean of the figures given by other experimenters gives  $5.1 \times 10^{-3}$  for the average of various sedimentary rocks, including slates, limestones, flagstones, and sandstones. As the great majority of gradient determinations have been made in sedimentary rocks, it would seem that we should, in estimating the flow of heat, use a value of  $K$  between  $5 \times 10^{-3}$  and  $6 \times 10^{-3}$ , and probably not greater than  $5.5 \times 10^{-3}$ . This would, with the actual gradient, yield a heat-flow of  $16.5 \times 10^{-7}$  calory per second per square centimetre. The heat-flow for a layer 40 kilometres thick, as calculated above, is  $25 \times 10^{-7}$ . For thicker or thinner layers the flow would be greater. Thus a flow of at least  $8.5 \times 10^{-7}$  calory per second remains to be accounted for. It seems probable that, owing to the fall of conductivity with increase in temperature, the value,  $4 \times 10^{-3}$ , previously assumed for the conductivity of the layer is fairly close to the mean value; but the change of conductivity with temperature would of course render the gradients less steep in the upper parts, and steeper in the lower parts, than those which would be obtained from the formula given above.

#### *Effect of Underground Water.*

The most obvious suggestion is that the effective conductivity of the surface layers may be augmented by underground water. The great majority of underground temperature observations have been made in bore-holes for wells, or in mines, which generally are to be found in more or less pervious strata. The quantity of water usually occurring in the latter may be judged by the fact that in England about 12 tons of water have to be pumped out for every ton of coal mined\*.

The true thermal conductivity of water being very small,

\* Sherlock, 'Man as a Geological Agent,' p. 285.

upward transference of heat in it will occur chiefly either by convection currents in "stagnant" water in pores, pockets, and fissures in the rock, or by flowing water, which sinks into the ground to reappear elsewhere as a deep-seated spring with an elevated temperature.

Experiments on the magnitude of the effect to be expected from convection are at present in progress, and will be described in a subsequent paper. The effect, especially in single water columns, is evidently extremely complex, the distribution of the convection currents apparently being very susceptible to accidental disturbances. A summary of the results so far obtained follows.

For gradients of about  $0.3^\circ$  per cm. the "Convectivity" (*i.e.* the vertical heat-flow per sq. cm. divided by the gradient) varies with the diameter and also with the length of the water column used, the extreme values recorded being about 0.3 for a tube 10.25 cm. long by 1.08 cm. diameter, and 2.3 for a tube 23.0 cm. long by 2.03 cm. diameter. Thus for columns of such sizes the convectivity at this gradient is of the same order as the conductivity of copper.

For smaller gradients the convectivity decreases rapidly, being roughly proportional to the 6th power of the gradient for each of two tubes 1.08 cm. diameter, to the gradient for the tube 2.03 cm. diameter, and to the square root of the gradient for two tubes 2.8 cm. diameter. Thus for the smaller isolated cavities and pores in rocks we should expect the convectivity to be negligible for the gradient existing in the earth. A cylindrical column of water 25 cm. deep by 3 cm. diameter should have a convectivity about 0.1, if we may extrapolate the results obtained down to such a small gradient. Larger cavities might be expected to act as better conductors of heat.

There was some evidence that in single columns the convectivity obtained a maximum at about  $17^\circ\text{C}$ . This is rather surprising, as, owing to the increased coefficient of expansion and decreased viscosity, we should expect a large increase in convectivity with rise in temperature. This increase was amply verified in the case of a double tube forming a circulating system, in which the ascending and descending currents were prevented from mixing. It is probable that the fall in convectivity observed with a single tube at temperatures over  $17^\circ\text{C}$ . is to be ascribed to increased mixing of the currents. As the effect of temperature in single columns is somewhat uncertain, and does not appear to be very great over the range ( $10^\circ$ – $20^\circ\text{C}$ .) covered by the experiments with various gradients, no allowance has been made for it in

arriving at the conclusions given above, which may be taken as referring to about  $14^{\circ}\text{C.}$ , the mean temperature of the water in the various tests.

With a double column consisting of two vertical tubes, each about 23 cm. by 1.08 cm., forming a closed water circuit, the results were much more consistent. The convectivity for a given gradient was, over the range covered, approximately proportional to the excess of the mean temperature above  $5^{\circ}\text{C.}$  (as was to be expected from a consideration of the variation of the coefficient of expansion, and viscosity, with temperature); and so the various results with different gradients could all be reduced to the mean temperature  $14^{\circ}\text{C.}$  The reduced convectivity varied from 8.31 for a gradient of  $0.30^{\circ}$  per cm. to 0.435 for a gradient of  $0.0124^{\circ}$  per cm., being approximately proportional to the 0.87th power of the gradient. Extrapolating the results down to earth gradient, we find 0.02 for the convectivity. Tests remain to be made with double tubes of other dimensions, but there can be little doubt but that larger tubes will show greatly increased convectivities, and smaller tubes negligible convectivities at earth gradients.

It would seem probable, then, that wherever water occurs in fissures more than a few square centimetres in area, or especially in fissures forming circulating systems, the upward transference of heat by it would be very appreciable, but that we would hardly expect that water in minute pores would appreciably increase the effective conductivity of the rock for the gradient obtaining underground.

As regards flowing water, it would seem that, in certain cases, very considerable quantities of heat may thus be brought to the surface. An examination of the figures for 147 deep wells in the United States\*, varying from 400 to 3350 feet deep, with flows ranging from 0.1 to 5500 American gallons per minute, shows that the average flow per well was 311 gallons per minute at about  $16^{\circ}\text{F.}$  above air temperature, the average depth being 1023 feet. This means that the average well was bringing to the surface about  $1.75 \times 10^5$  calories per second, which would represent a flow of  $8.5 \times 10^{-7}$  calory per sq. cm. per second over an area of about 20 square kilometres per well. It is hard to say how this heat-flow will fall with time, but in the case of natural springs very large quantities of heat are continuously brought to the surface over long periods of time. For example, the hot springs at Bath represent a heat-flow

\* United States Geological Survey Water Supply Paper, No. 57.

of about  $8.5 \times 10^5$  calories per second, *i. e.* enough to provide the flux-density required over an area of 100 square kilometres, and do not appear to have varied much for many years. It is possible that some of this heat may be due to a local concentration of radioactive matter, as the Bath water, like many deep-seated springs, shows considerable radioactivity.

If, of the total rainfall in any locality, a quantity equivalent to one inch per annum sank into the ground to such a depth that it emerged with its temperature raised by  $1^\circ \text{C.}$ , the corresponding heat carried off would be about  $0.8 \times 10^{-7}$  calory per second per square centimetre. It would thus seem to be probable that part of the discrepancy might be attributed to flowing water.

#### *Effect of Secular Variations in Climate.*

It seems to be worth while to consider what the effect of possible slow climatic changes would be. The retreat of glaciers, which at present appears to be occurring in most parts of the world, would apparently indicate a slow increase in the average temperature. In Europe and North America, where the majority of earth-temperature measurements have been made, this change is generally considered to have progressed more or less continuously since the last ice age.

Let us assume that the surface temperature is undergoing a secular harmonic variation of amplitude  $\alpha$  and periodic time  $T$ . Then, if there were no subterranean source of heat, the temperature  $\theta$  at a depth  $x$  and a time  $t$  would be given by the well-known equation

$$\theta = \theta_0 + \alpha e^{-\frac{2\pi x}{\lambda}} \sin 2\pi \left( \frac{t}{T} - \frac{x}{\lambda} + \frac{\gamma}{2\pi} \right).$$

Here  $\theta_0$  is the average surface temperature;  $\lambda$ , the wavelength of the temperature waves, is equal to  $\sqrt{4\pi kT}$ , where  $k$  is the diffusivity; and  $\gamma$  is a phase angle. Since  $e^{-2\pi}$  is approximately equal to  $1.9 \times 10^{-3}$ , it is evident that at a depth  $\lambda$  the variations of temperature would be negligible, and the temperature always approximately equal to  $\theta_0$ .

During the last glacial epoch the southern edge of the ice field apparently passed through the South of England, where the summer temperature is now about  $15^\circ \text{C.}$  When under ice the ground temperature can never have exceeded  $0^\circ \text{C.}$ , so possibly  $15^\circ \text{C.}$  is a fair figure to assume for the rise which has occurred.

If we assume that at present the surface temperature is equal to the secular mean,  $\theta_0$ , we see that we must put

$$\alpha = 15^\circ \text{C. and } \frac{t}{T} + \frac{\gamma}{2\pi} = 0.$$

Thus  $\theta = \theta_0 - \alpha e^{-\frac{2\pi x}{\lambda}} \sin \frac{2\pi x}{\lambda}$

and  $\frac{\partial \theta}{\partial x} = \frac{2\pi \alpha}{\lambda} e^{-\frac{2\pi x}{\lambda}} \left[ \sin \frac{2\pi x}{\lambda} - \cos \frac{2\pi x}{\lambda} \right].$

There would thus be a temperature minimum at a depth  $\frac{\lambda}{8}$  below the surface, the temperature being  $\frac{\alpha e^{-\frac{\pi}{4}}}{\sqrt{2}}$ , i. e.  $0.323 \alpha$

below that at the surface. Taking the thermal conductivity as  $5.5 \times 10^{-3}$ , the density as 2.7, and the specific heat as 0.19, we find that  $k = 1.07 \times 10^{-2}$ , and hence  $\lambda = 0.37\sqrt{T}$ . The value to be assigned to  $T$  will vary with the date assumed for the middle of the last glacial epoch, about which there appears to be very great uncertainty. If we place this 20,000 years ago, we must put  $T = 80,000$  years or  $2.52 \times 10^{12}$  seconds, which makes  $\lambda$  nearly equal to 6 kilometres. The temperature gradient would be  $-1.6 \times 10^{-4}$  degree per centimetre at the surface, falling to zero at a depth of 750 metres, below which there would be a very small positive gradient. The excess of temperature,  $\delta\theta$ , at the surface over that at a depth  $x$  metres would be as follows:—

$x \dots$	100	200	300	400	500	600	700	800	900	1000
$\delta\theta \dots$	1.4	2.5	3.4	4.0	4.4	4.7	4.8	4.8	4.7	4.6^\circ \text{C.}

The actual temperature variation with depth would of course be obtained by superposing the above figures on the uniform positive gradient due to the escape of heat from the interior.

Thus the effect of the secular variation assumed above would be to reduce the actual gradient for the first few hundred metres by a quantity of the order of  $1^\circ$  per hundred metres, which would go far towards reducing the discrepancy in the heat-flux. An increase in gradient with depth appears to have been clearly established in deep borings\*. We may note that the depth at which any given value of  $\delta\theta$  occurs is proportional to  $\sqrt{T}$ , so that if we were

\* Daly, Am. Journ. Sc., May 1923, p. 354.



to make  $T=320,000$  years, the corresponding depths would all be doubled, and the effect on the temperature gradient would be halved.

If, however, we assume that during the last few hundred thousand years the mean temperature  $\theta_0$  has been  $7\frac{1}{2}^\circ\text{C}$ . below the present average, and that the harmonic variations giving rise to successive glacial periods were of amplitude  $7\frac{1}{2}^\circ\text{C}$ ., so that at present we are enjoying a temperature maximum, or, at least, have reached a temperature equal to the previous maxima, we must evidently, for the present

day, put 
$$\frac{t}{T} + \frac{\gamma}{2\pi} = \frac{1}{4}, \quad \text{and} \quad \alpha = 7\frac{1}{2}^\circ\text{C}.$$

Then 
$$\theta = \theta_0 + \alpha e^{-\frac{2\pi x}{\lambda}} \cos \frac{2\pi x}{\lambda},$$

and 
$$\frac{\partial \theta}{\partial x} = -\frac{2\pi\alpha}{\lambda} e^{-\frac{2\pi x}{\lambda}} \left[ \sin \frac{2\pi x}{\lambda} + \cos \frac{2\pi x}{\lambda} \right].$$

Thus the minimum temperature would now occur at a depth

$\frac{3\lambda}{8}$ , the temperature being  $\alpha \left[ 1 + \frac{e^{-\frac{3\pi}{4}}}{\sqrt{2}} \right]$ , i. e.  $1.067 \alpha$  below

that at the surface. If, as before, we make  $T=80,000$  years, and consequently  $\lambda=6$  kilometres, we must date the middle of the last glacial period 40,000 years ago. The minimum would now occur at a depth of 2250 metres, the temperature being  $8^\circ\text{C}$ . below that at the surface. The distribution of temperature with depth would now be as follows:—

$x \dots$	200	400	600	800	1000	1200	1400	1600	1800	2000	2200	2400
$\theta \dots$	1.6	3.0	4.3	5.3	6.2	6.8	7.3	7.7	7.9	8.0	8.0	8.0

The effect would thus be to reduce the actual gradient by about  $0.6^\circ$  per 100 metres for the first 1000 metres, with smaller reductions for greater depths. The variation of gradient with depth to be expected on this hypothesis would be less noticeable than on the previous one; while the estimate of the heat-flow from the lower parts of the crust would have to be increased by some 20 per cent. to allow for the effects of climatic changes, the excess being used up in raising the temperature of the upper layers in conformity with the general increase of surface temperature.

*Heat Evolved during Volcanic Eruptions.*

Immense quantities of heat are brought to the surface during violent eruptions, but these are so uncommon both in time and locality that their effect on the average loss of heat is probably small. It could hardly, however, be classed as absolutely negligible. The volume of the lava poured out during the eruption of Skapta Jokul in 1783 has been estimated at 25 cubic kilometres. This would mean the liberation of about  $2 \times 10^{19}$  calories—as much heat as would be generated in a century by a layer of rock of the assumed radioactivity 10 kilometres thick and covering an area of a million square kilometres. It is difficult to say to what extent this heat is to be ascribed to the continental rocks, and to what extent to the underlying magma.

During revolutionary periods immensely greater quantities of lava are extruded, mostly derived from the underlying magma. As the equilibrium temperature of the central parts of the thicker layers of continental rocks would be expected to be considerably above the melting-point of basalt, we would expect these great flows to reduce the temperature of these layers very considerably, so that during the intervening stable periods the temperature of the continental masses would be slowly rising again. Thus our assumption of constant temperature would have to be modified, and the heat-flux to be expected at the surface correspondingly reduced.

*Conclusions as to the Reality of the Gradient Discrepancy.*

It has been pointed out above that there are several factors affecting the gradient near the surface, and that every factor would be expected to produce an appreciable lowering of the gradient. We do not possess sufficient data to enable us to calculate the actual magnitude of the effects to be expected, so that it does not seem to be possible to quantitatively explain away the discrepancy. As, however, all the factors act in the same direction, it is not surprising that the actual gradient is considerably smaller than we would expect to find it, if their effects were absent.

We are thus led to the conclusion that the smallness of the gradient just below the surface cannot be regarded as any evidence against the occurrence of radioactivity, similar to that of surface rocks, throughout the whole depth of the continental masses.

*Accumulation of Heat below the Continental Masses.*

We have seen above that we should expect a downward flow of heat at the base of any continental mass exceeding 40 kilometres thick. Even with somewhat thinner layers there would be very little upward flow from the underlying magma, which would accordingly accumulate heat energy faster than similar magma at an equal depth below the ocean. We should thus expect fusion of the magma to occur much sooner beneath the continents than elsewhere. This comparatively light liquid magma would tend to find its way towards the surface, by flowing upwards along the sloping lower surface of the continental mass towards its thin edges. This may have some connexion with the prevalence of volcanoes along continental margins.

By the time that a sufficiently world-wide accumulation of heat had occurred to usher in a revolution, we should expect to find the continents floating on vast masses of liquid magma, probably at a temperature above the average. Even if the ocean floor remained sufficiently rigid during a revolution to prevent the relative motions of the continents suggested by Wegener, we should still expect tidal forces to produce an east to west motion of the crust as a whole relative to the core during these periods. The continents would thus drift away from the magma which previously underlay them.

It seems almost certain that the subsequent resolidification of the magma would take place from below upwards. The crustal motion would thus ultimately be arrested by the "grounding" of the deeper continental masses on solidified magma. It is conceivable that large localized tangential stresses might thus be set up which might cause the intense horizontal compression often evident in mountainous areas\*.

At the close of the cycle, then, we should find the contents resting on solidified magma, whose latent heat of fusion would form a sink for the heat flowing downwards from the overlying continent for ages to come.

*Summary.*

A consideration is given of the temperature distribution in a uniform layer of solid rock of radioactivity equal to that of the Earth's surface materials, and whose lower surface is at the melting-point of basalt. Figures are given for the

\* This is only another way of looking at an idea already suggested by Dr. Joly.

maximum temperature to be expected, on certain assumptions, for layers of different thicknesses. The following factors, which affect the temperature gradient near the surface, are considered :—

- (1) Variation of thermal conductivity with temperature.
- (2) Effect of underground water. Some results of experiments on convection in vertical water-columns show that we might expect large effects with water in fissures of moderate size, but only very slight effects with pores.
- (3) Secular variation of climate.
- (4) Heat evolved during volcanic eruptions.

As it is shown that all these effects conspire to reduce the temperature gradient, it is contended that the smallness of the latter is no evidence against the uniform distribution of radioactivity throughout the continental layer.

It is suggested that owing to tidal stresses and consequent crustal motions the continents towards the end of revolutionary periods become "stranded" on solidified magma, and that during inter-revolutionary periods the heat evolved in their lower layers is largely used in re-melting this magma.

Royal Dublin Society  
June 8, 1923.

*XLII. Grouping of the Lines of the Secondary Spectrum of Hydrogen. By K. BASU\*.*

**T**HE problem of the secondary spectrum of hydrogen continues to be as interesting as ever, as can be easily seen from the large number of experimental and theoretical papers appearing on the subject. It seems now to be fairly well established that the secondary spectrum is due to the molecule of hydrogen. But we are still in the dark about the mechanism underlying the combination of two Bohr-hydrogen atoms to form the molecule and the genesis of radiation in the process. In considering the process of combination of two atoms which, according to Langmuir, is attended with the evolution of 82,000 calories of heat per gm.-molecule, it is often assumed that a molecular spectrum is emitted, the limiting frequency of which is given by the Bohr relation

$$h\nu = W \quad (\text{heat evolved}).$$

\* Communicated by Prof. Megh Nad Saha.

The assumption is based upon the analogy of the origin of the atomic spectrum. We know that when one electron combines with an ionized atom, the atomic spectrum is produced. If  $W$  is the heat of ionization, the limiting frequency of the atomic spectrum is given by the relation

$$h\nu = W \quad (\text{heat of ionization}).$$

But a little consideration will show that this law cannot hold in the case of molecular dissociation. For then the limiting frequency of the molecular spectrum of hydrogen would lie at  $\lambda = 3600 \text{ \AA.U.}$  But the fact that ordinary  $\text{H}_2$ -gas is quite transparent to radiation of this wave-length shows that Bohr's rule cannot be applied to any case of molecular dissociation. The secondary spectrum extends to about  $\lambda = 3300$ , which is also against Bohr's rule, provided this spectrum is regarded as the molecular spectrum.

It is also evident that in view of the enormous number of lines in this spectrum, any attempt at grouping will meet with a certain amount of success, which, after all, may turn out to be quite fortuitous.

The laws are expected to be more complicated than in the case of line spectra, since the distance between the nuclei must, as a matter of course, occur in the formula. An attempt was made to see if any of the lines may be regarded as due to  $\text{H}_2^+$ , i. e. two hydrogen nuclei at a definite distance  $l$  cm. from each other with an electron revolving about them. The case has been already treated by F. Tank (*Ann. d. Phys.* Bd. lix.) and L. Silberstein, because the dynamics can be handled by the Hamilton-Jacobian method, but it has not been applied to the case of the secondary spectrum. Using Bohr's rule, the frequency comes out in the form

$$\nu = 4N \left[ \frac{1}{(n_1 + n_2 + \Delta n_2)^2} - \frac{1}{(n_1' + n_2' + \Delta n_2')^2} \right],$$

where  $N$  = Rydberg number,  $n_1, n_1'$  are azimuthal quantum numbers,  $n_2, n_2'$  are radial quantum numbers, and

$$\Delta n_2 = 16\pi^4 l^2 m^2 e^4 / h^4 n_2^3.$$

Thus  $\Delta n_2$  involves the distance between the nuclei. The value of  $l$  can only be guessed. Let us assume  $l = 1 \times 10^{-8} \text{ cm.}$ , which is slightly less than  $2a$ ,  $a$  = radius of the Bohr H-atom.

Then

$$\nu = A - \frac{4N}{\left( n_1 + n_2 + \frac{3 \cdot 55}{n_2^3} \right)^2}.$$

Let us classify the lines under the following heads :—

- (i.) For  $n_2 = 1$ ,  $\nu = A_{1\infty} - \frac{438710.76}{(n_1 + 4.55)^2}$  ;  
 (ii.) For  $n_2 = 2$ ,  $\nu = A_{2\infty} - \frac{438710.76}{(n_1 + 2.44)^2}$  ;  
 (iii.) For  $n_2 = 3$ ,  $\nu = A_{3\infty} - \frac{438710.76}{(n_1 + 3.13)^2}$  ;  
 (iv.) For  $n_2 = 4$ ,  $\nu = A_{4\infty} - \frac{438710.76}{(n_1 + 4.055)^2}$  ;  
 (v.) For  $n_1 = 0$ ,  $\nu = B_{0\infty} - \frac{438710.76}{\left(n_2 + \frac{3.55}{n_2^3}\right)}$  ;

where  $A_{1\infty} = 21191.16$ , obtained by putting  $n_1 = 0$  in the second term of the right-hand member of (i.) ; in the same way  $(A_{2\infty}, A_{3\infty}, A_{4\infty}, B_{0\infty}) = (22254.17, 25720.5, 26680.6, 21191.91)$ , when we put respectively  $n_1 = 2, 1, 0, 0$  in the corresponding second terms of the right-hand members of (ii.), (iii.), (iv.) and (v.).

For the First Series :

$A_{1\infty}$	$n_1$	$\nu_{\text{cal.}}$	$\nu_{\text{obs.}}$
21188.91	10	19116.86	19116.92
"	11	19374.86	19372.41
"	12	19587.41	19584.89

For the Second Series :

$A_{2\infty}$	$n_1$	$\nu_{\text{cal.}}$	$\nu_{\text{obs.}}$
22254.17	10	19419.27	19411.74
"	11	19825.47	19829.35
"	12	20060.00	20061.11

For the Third Series :

$A_{3\infty}$	$n_1$	$\nu_{\text{cal.}}$	$\nu_{\text{obs.}}$
25720.5	10	23175.75	23179.81
"	11	23523.15	...
"	12	23804.04	23804.13

For the Fourth Series :

$A_{4\infty}$	$n_1$	$\nu_{\text{cal.}}$	$\nu_{\text{obs.}}$
26680.6	10	24459.77	24456.46
"	11	24243.78	...
"	12	24978.6	24976.76

For the Fifth Series :

$B_{0\infty}$	$n_2$	$\nu_{\text{cal.}}$	$\nu_{\text{obs.}}$
21186.81	10	16802.44	16802.38
"	11	17562.11	17562.35
"	12	18141.33	18140.19

But the above coincidences, though interesting, can hardly be claimed to have solved the problem of the molecular spectrum, because the distance between the nuclei has been taken

arbitrarily. If some other value were assumed, we should probably get some other coincidences.

In view of the fact that we are yet far removed from the satisfactory solution of the coupling of two Bohr H-atoms to form an  $H_2$ -molecule, which is by far the simplest problem of this class we can think of, is it not a bit too premature to attempt the general solution of the problems of chemical combination of more complicated atoms like Na and Cl, as has been done in the theories of Lewis and Langmuir? To the same category must belong the large number of radiation theories of monomolecular reaction, which are all based upon the Bohr rule  $h\nu = \text{heat of dissociation}$ .

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XLIII. *The Absorption of Light by Sodium Vapour.* By  
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[Plate VIII.]

### 1. INTRODUCTION.

THE normal operation of an arc below ionization results in the excitation of the first line of the principal series, providing that the energy of the electrons is equal to, or greater than, the resonance potential. As the accelerating potential in the arc is increased, the intensity of this line increases, approximately proportional to the total number of electrons, until the ionization potential is reached. At this point there should be, according to the Bohr theory of the atom, a pronounced decrease in the intensity of the line, and this decrease takes place at the voltage at which the complete line spectrum is produced. The line  $1.5\text{ S}-2p$  is the result of inelastic collision with electrons having energy equal to the resonance potential, but as this voltage is exceeded, electrons which at a slightly lower value would give rise to this line, now produce the complete spectrum. Any line of the series  $1.5\text{ S}-mp$ , where  $m$  is greater than 2, is necessarily excited at the sacrifice of the line  $1.5\text{ S}-2p$ . After a certain voltage has been reached, however, the intensity of any line per unit number of electrons present per c.c. attains a saturation value, in agreement with the quantum theory, for the number of quanta radiated is proportional to the number of

\* Communicated by the Author.

collisions, and hence, approximately, to the number of electrons present.

In a previous communication by the author \* it has been shown that under certain physical conditions in the sodium vapour arc, the D lines of sodium are relatively much brighter than the lines of the subordinate series, although of course these latter lines are always much fainter than the D lines. In this work the applied potential difference was so large that the saturation value of the intensity of any line must have been attained, and the effect was explained by the self-reversal of the subordinate series lines. The atoms of sodium vapour in this case must be in an abnormal state, by which is meant that the valency electron, instead of being in the 1.5 S stable orbit, must be displaced to the first *p* ring. This condition can be brought about by an electrical stimulus, the density of the electrons being very great. Then the energy necessary for the displacement of the electron to the first *p* ring may be obtained either by direct impact with electrons possessing the requisite resonance potential, or it may be absorbed as radiation emitted by neighbouring atoms in which the electron is temporarily in the first *p* ring. At high vapour-pressure and considerable current density, it is probable that most of the energy in the abnormal atom is derived from the second of these sources. Under ordinary conditions nearly all the atoms of a vapour exist in the normal state, and the value of the energy is a minimum. Light corresponding to a given line in the spectrum will be absorbed when the atoms pass from this state to a state in which the electron revolves in one of the *p* rings. Unexcited sodium vapour shows, therefore, absorption corresponding to the principal series lines only. If, however, the atoms can be brought to the condition that a considerable proportion have the electron in the 2*p* ring, then the radiation absorbed when white light is passed through the vapour will be the lines which in the emission spectrum arise when the electron is displaced from the 2*p* ring to outer stationary orbits, *i. e.* the subordinate series lines.

It appears probable that this abnormal state of the vapour can be produced not only by electrical stimulation, but also by high temperature, for King † observed absorption in the subordinate series lines of the alkalis with his electric furnace. Using a special plug at the centre of the tube, by which temperatures above 3200° C. could be obtained, and excluding oxygen, these absorption lines in the subordinate

\* Phil. Mag. vol. xlv. (1923).

† Phys. Rev. vol. xviii. (1921).



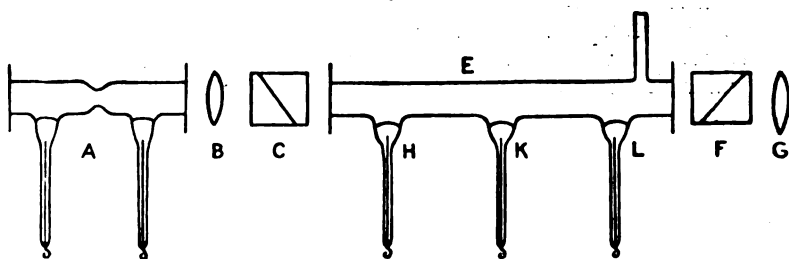
series exhibited sharpness and freedom from dissymmetry, so that their wave-lengths could be accurately measured. The temperature required is very high, much higher than that used when the absorption of the principal series lines is observed; and it is possible that the atoms will only begin to absorb the subordinate series lines when they are nearly hot enough to emit the lines of the principal series. A thermal or electrical stimulus can cause the electron to assume one of the stationary orbits, and as Saha\* has pointed out, the temperature necessary to ionize atoms is probably approximately proportional to the ionization potential. This would explain the absence of certain elements in the sun. The temperature in the latter is so high that the atoms of these missing elements are completely ionized, and so the lines due to the ionized atom only would be present, and in the majority of cases these lie in the ultra-violet region.

The present work forms a continuation of that described in the previous paper.

## 2. EXPERIMENTS.

In the previous work a sodium-potassium alloy vapour arc lamp had been used, and the light from a constriction in it had been viewed after passing along a wider portion of the lamp. By this means the bright radiation had passed through

Fig. 1.



a column of feebly luminous sodium vapour, and a marked decrease in the brightness of the subordinate series lines, relative to that of the D lines, was noted. The apparatus used in the present experiments is shown in fig. 1.

The sodium-potassium alloy vapour arc lamp A was arranged so that the constriction was horizontal and endways on. The radiation, made parallel by a lens B, passed through a nicol prism C, and then through the quartz tube E acting as a sodium vapour arc lamp. Emerging, the light was

\* Phil. Mag. vol. xlv. (1922).

transmitted through another nicol prism F, and it was then brought to a focus at the slit of the collimator by means of the lens G. The ends of the quartz tube E were closed by quartz plates, and three electrodes were arranged so that the arc could be struck between H and K, or it could be lengthened so as to pass between H and L. The distance between H and K and between K and L was about 10 cm. E was placed within an electric heater, the ends of the tube projecting beyond the heater to keep the wax from melting, and, as an extra precaution, the wax was water-cooled. The temperature was measured with a mercury thermometer placed within the electric heater. Pieces of sodium had been placed at H, K, L, and the lamp E was kept highly exhausted.

The electric arc is much more difficult to maintain with sodium than it is with the alloy of sodium and potassium, and it requires a much greater applied potential difference before it will strike. Whereas the lamp containing the alloy would work with as small a potential difference as 40 volts, 100 volts was required for the sodium lamp, and it had to be maintained highly exhausted before it would work successfully. If the vapour-pressure of the sodium became too great the lamp would not work. The arc when struck did not fill the tube completely, but confined itself to the lower part of the tube, so that the upper portion was filled with sodium radiation much less intense in brightness than in the actual arc. This was very convenient, as it enabled the radiation from A to be passed through E without being masked by the intense sodium arc.

When the nicol prisms were crossed, the radiation from E alone entered the spectroscope, and by rotating C the intensity of the light entering the spectroscope could be varied.

The lamp A was of quartz with a constriction at the centre, the distance between the two electrodes being about 10 cm. The arc was struck by heating the alloy with a bunsen burner, and then passing a weak discharge from a small induction coil through the vapour. The spectrum from this type of lamp showed the potassium lines much brighter than they were in the lamp previously described by the author\*. The older form was much smaller, and, as a result, when once the arc was struck, the temperature increased rapidly and the vapour-pressure became fairly large. When an electric discharge, or any electric current, is passed through a mixture of sodium and potassium vapours, the sodium lines

\* Phil. Mag. vol. xliv. (1922).

always predominate unless the partial pressure of the potassium is many times greater than that of the sodium. So in the present case, when the arc was first struck, the potassium lines were very strong, particularly at the ends of the lamp where the temperature, and so the sodium vapour-pressure, were low. At the constriction the potassium lines were faint. The pair  $\lambda 4642$  was very prominent although it has the series notation  $1.5S-2d$ . This line appears bright with heavy currents—5 amps. per sq. cm.—and is shown in Pl. VIII. (II.).

With high current density a continuous spectrum was emitted, beginning at  $\lambda 7000$  and ending at  $\lambda 5480$ , and also extending from  $\lambda 4980$  to the ultra-violet region, the first portion being by far the strongest. As the current density was decreased, the line spectrum became more prominent and the continuous spectrum less so. Another interesting feature of the lamp was the production of an emission fluting spectrum. These bands appeared at all current densities, but were particularly bright when the current density was small. They could be divided into four groups, and although they were equally spaced in a group, this spacing varied in the different groups. The heads of the bands were situated between the limits  $\lambda 6700$  and  $\lambda 5500$ .

When light from the lamp A was passed through the unexcited sodium vapour in E there was considerable reversal of  $\lambda 5890$ ,  $\lambda 5896$ , but no apparent effect on any other line in the spectrum. Striking the arc in E and passing the radiation from A through the feebly luminous sodium vapour in E, the subordinate series lines of sodium decreased very much in brightness, although there was, as far as could be judged visually, no change in the intensity of the potassium lines. This is shown in Pl. VIII. (I. & II.), the exposures being the same in each spectrogram. The effect was most marked when the temperature of the lamp E, as measured by the thermometer, was  $150^{\circ}\text{C}$ . It is certain, however, that the actual temperature in the lamp itself must have been greater than this, owing to the passage of the arc. At higher temperatures the vapour-pressure of the sodium within E became too large, and prevented the arc from being struck. This decrease in intensity was most marked when the arc in E passed between the electrodes H and L.

When the radiation from A was sent through the intense light within E no definite result was obtained, as the luminosity within E was brighter than that from A.

A carbon arc was now substituted for the lamp A, and an

attempt made to reverse the subordinate series lines of sodium on a continuous spectrum. There was no apparent reversal when the white light was passed through the intense radiation in E, but when it was sent along the top part of the tube so that it was transmitted through the feebly luminescent sodium vapour, marked absorption of  $\lambda$  5688,  $\lambda$  5683, and feeble absorption of  $\lambda$  6161,  $\lambda$  6154 was noted. In addition, there was considerable absorption of  $\lambda$  5896,  $\lambda$  5890, showing that in the feebly luminous vapour there were many atoms in the normal condition. This is shown in Pl. VIII. (IV.). The temperature of the sodium vapour in E as measured by the thermometer was  $150^{\circ}\text{C}.$ , and the arc passed between H and L.

The alloy of sodium and potassium was now substituted for the sodium in E, and the arc passed between H and L. Examining the radiation from A after it had been transmitted through the feebly luminous portion of E, showed that all the lines of sodium and potassium except  $\lambda$  5896,  $\lambda$  5890 became much fainter, Pl. VIII. (III.)

From these experiments it is concluded that electrically luminescent sodium and potassium vapours show different absorption of light effects from those exhibited by the normal vapours, and these effects are produced by atoms in an abnormal state, the valency electron being in the first  $p$  ring instead of the  $1.5\text{S}$  orbit.

### 3. SUMMARY.

1. The radiation from a sodium-potassium alloy vapour arc lamp was sent through feebly luminous sodium vapour. The subordinate series lines of sodium decreased in intensity.

2. White light from an electric arc passed through this feebly luminous sodium vapour showed absorption of  $\lambda$  6161,  $\lambda$  6154,  $\lambda$  5688,  $\lambda$  5683 lines belonging to the subordinate series.

3. These effects are explained by the presence of atoms in an abnormal state, this state being brought about by an electrical stimulus. The valency electron of these atoms is in the first  $p$  ring.

XLIV. *On the Polarization of the Light scattered by Gases and Vapours.* By C. V. RAMAN, M.A., D.Sc. (Hon.), Palit Professor of Physics in the Calcutta University, and K. SESHAGIRI RAO, M.A., University of Madras Research Scholar\*.

### 1. Introduction.

THE work of Lord Rayleigh† and others has shown conclusively that the light scattered transversely by gases is not in general perfectly polarized, but shows a defect of polarization which at the ordinary temperature and pressure is characteristic of each gas. This result is of great interest, and has been interpreted as due to the optical anisotropy of the scattering molecules, which is different for different gases. Observation shows that with monatomic gases such as argon the scattered light is almost completely polarized, while more complex molecules show a very marked imperfection of polarization. The exact measurement of the state of polarization of the scattered light for different gases, and of its variations with temperature, pressure, and the frequency of the incident light, is an experimental problem of the first importance. Preliminary measurements were published by Rayleigh, Cabannes, and Gans. These disagreed considerably among themselves; the most reliable data that have so far appeared are those obtained in Rayleigh's own later work, in which some very careful measurements were made with special precautions to secure accuracy. The table given below collects the data referred to, the last column showing Rayleigh's definitive measurements. The figures give the ratio of the weak to the strong component of polarization as a percentage.

	Rayleigh. I.	Cabannes.	Gans.	Rayleigh. II.
Argon .....	...	0.8	...	0.46
Hydrogen .....	1.7	1 to 2	...	3.83
Nitrogen .....	3.0	2.5 to 2.8	3.0	4.06
Air.....	4.2	3.7 to 4.0	...	5.0
Oxygen .....	6.0	5.1 to 5.4	6.7	9.4
Carbon dioxide.....	8.0	9.5 to 9.9	7.3	11.7
Nitrous oxide .....	14.0	...	12.0	15.4

\* Communicated by the Authors.

† Rayleigh, Proc. Roy. Soc. vol. xcv. p. 155; vol. xcvi. p. 435; vol. xcvi. p. 57. Cabannes, *Ann. der Physique*, tome xv. pp. 1-150. Gans, *Ann. der Physik*, lxx. p. 97 (1921).

Rayleigh in his experiments used a photographic method. Each measurement required several exposures, each of several hours' duration. Direct *visual* measurements of the state of polarization, if they were possible, would obviously be much more expeditious, and would enable a large number of gases and vapours to be examined. It was with the object of determining whether accurate measurements were possible by visual methods and to find the influence of the frequency of incident radiation that the present work was undertaken, and the paper describes the results so far obtained.

While dealing with this subject, it should be mentioned, as has been already remarked by one of us elsewhere, that in the case of dense gases and vapours *not* obeying Boyle's law, the state of polarization of the scattered light should not be independent of the temperature and pressure. In fact, when the scattering is greater than in proportion to the density, the scattered light should be more perfectly polarized. Observations with carbon dioxide under pressure, ether, benzene, and pentane vapours entirely confirm this indication of theory.

## 2. *Experimental Arrangements.*

In order that visual measurements might be possible, very intense illumination is obviously required. This was obtained with the aid of a powerful optical combination of an astronomical telescope of 18 cm. aperture and 200 cm. focal length and a converging lens placed beyond its focus. A beam of sunlight which fills the object-glass of the telescope and passes through the combination is converged by it into an extremely intense beam of a few millimetres diameter but of small angle. With such intense illumination, the scattering of light by gases and vapours becomes a very conspicuous phenomenon, and is of a brilliant sky-blue colour. With the help of a double-image prism it is easy to observe visually that the transversely scattered light is not completely polarized.

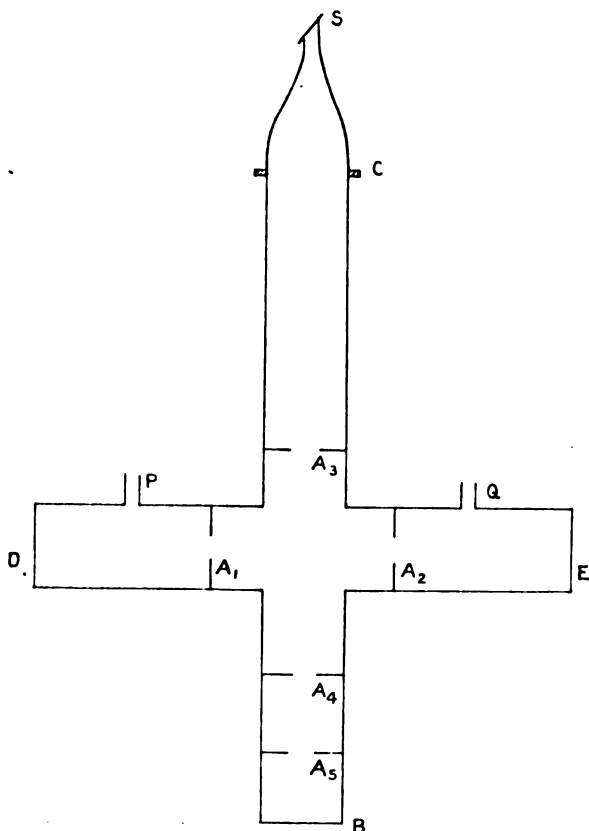
As in Rayleigh's experiments, the gas is contained in a vessel in the form of a cross-tube, the primary beam passing along one arm and the scattered beam being observed in the perpendicular direction. For accurate work the most important thing is of course the adequate blackness of the background, against which the faint light under investigation is to be observed. It is essential that special attention should be given to the way in which the far end of the vessel against which the observations are made is constructed.

It must be so arranged as to send back exceedingly little or, better still, no light at all. For, if the back of the tube returns any light, serious error will be introduced, for the visibility of the fainter track of the two seen through the double-image prism would be greatly diminished. In fact, preliminary experiments with a cross in which the background was not perfect gave invariably values for the intensity of the weaker component of polarization which were much too small. In his final experiments Rayleigh used a curved horn blown out of dark green glass and fitted to the far end of the observation tube. Any light which fell into the mouth of the horn was reflected internally from side to side towards the end away from the observing side. As such a horn was not available to us, other expedients had to be tried. The final arrangement adopted was to use a dark green conical glass bottle with its bottom cut out. The neck was ground down obliquely at an angle of  $45^\circ$ , and to this was cemented a dark glass plate. It was found that this gave quite a good background, and the use of sunlight, which gives beams of relatively small divergence, is specially favourable for avoiding stray illumination.

The cross-tube was made of zinc, and was 7 cm. in diameter. The arm to which the conical bottle was attached was about 36 cm. in length, and the other three arms were 25 cm. in length. The metal parts were all soldered together. The primary beam entered through the plate-glass window D, and passing through the circular diaphragms  $A_1$  and  $A_2$  of diameter 2 cm., fell on the window E. The laterally scattered light was observed through the window B. A diaphragm was placed at  $A_3$  so as to cut off any stray light getting inside. Apertures  $A_1$  and  $A_2$  served to cut off from view any stray light that fell on the edges of  $A_3$  and which tended to make these edges luminous as seen from the window. C is the glass bottle fixed to the observation arm. S is the dark glass plate cemented to the bottle at an inclination of  $45^\circ$ . The glass bottle was painted dead black outside and wrapped in black cloth as an additional precaution. The inside of the cross was completely painted dead black. The glass windows were fixed in position by screwing brass caps on to the ends of the tube. Thick rubber washers were placed between the metal and the glass so as to distribute the pressure and to make the whole airtight. The ends of the cap were further coated with a cement made of a mixture of rosin and wax so as to prevent any leakage. The air-tightness of the whole apparatus was tested, and it was found that there was a leakage of about

10 cm. of mercury in one hour. It was, however, thought not advisable to spend time in making it more perfectly air-tight, as the gas could be passed for a sufficiently long time to ensure that all air was driven out, and also as the observations were all made visually in a short time. P and Q are the ends for the entrance and exit of the stream of gas.

Fig. 1.



As mentioned above, brilliant sunlight concentrated by an 18-cm. aperture object-glass combined with a short focus lens was used. By suitable diaphragms stray light can be entirely cut off and prevented from entering the cross-tube. In order to make quantitative observations and to determine the ratio of the two components of polarization of scattered light, it is very essential that the eye should be

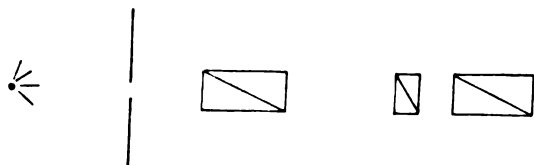


properly screened from all outside light and must be able to see only the two patches of light. For this purpose a small dark room made of thick canvas stretched on wooden supports was built up in front of the observation window of the cross-tube. A hole of just the size of the diameter of the cross-tube admitted a little of the observation arm of the cross into the room and the photometric apparatus—that is, the double-image prism and the nicol—were mounted within it. The room could be made perfectly dark, and when the eye had been for some time accustomed to the darkness, the two patches of light seen through the double-image prism could be easily made out. Even in the case of hydrogen, which scatters only about a fourth as much as air, there was no great difficulty experienced in seeing the two tracks.

The method employed to measure the imperfection of polarization was to use the double-image prism and a square-ended nicol. The double-image prism when properly oriented gave the two images, which had intensities in the same ratio as the polarized components of the scattered light. These two intensities were then equalized by the nicol. This method is very convenient, as continuous adjustments can be made. In working with the prisms, there are, as pointed out by Rayleigh, two possible sources of error. One is, that it might be possible that, starting with the unpolarized light, the double-image prism would not produce two images of equal intensity within the desired limits of accuracy, and hence the ratio of the intensities with partially polarized light could not be taken as a true measure of the constitution of the light; and the second is, that it might be possible that the  $\tan^2\theta$  law does not hold. For accurate determination it is therefore very essential to know that these sources of error do not conspire to produce errors beyond the desired limit of accuracy.

The following method was therefore adopted to test the

Fig. 2.



behaviour of the prisms. A ground-glass screen was illuminated by an electric lamp, and a black screen with a rectangular aperture was placed in front of it. The aperture gave perfectly unpolarized light, and could be viewed through

the double-image prism and nicol to be tested. In front of the double-image prism another nicol was mounted to polarize the light in any desired orientation, and the test was carried out by determining the ratio of the vertical and horizontal components of polarization of the beam transmitted through it in different orientations. Both nicols were mounted at the centres of accurately divided circles so that their orientations could be read off very accurately. Preliminary tests with the unpolarized light showed that the double-image prism produced images of practically equal intensity. The double-image prism was then adjusted so that the two images were just touching each other and were in a line. This secured that the direction of vibrations in the images were approximately horizontal and vertical. The polarizing nicol was then mounted in front of the double-image prism, and the orientations in which one of the two images vanished were noted. They differed by  $90^\circ$ , as was to be expected. The nicol was then set at a definite orientation  $\phi$  with the vertical, the double-image prism remaining fixed, and the ratio of the intensities of the vertical and the horizontal components in the beam passed by it was determined by rotating the second nicol and equalizing the brightness of the two images. The ratio was found to be  $\tan^2\phi$  without appreciable error.

Measurements were also made with a few vapours of organic liquids such as benzene, ether, and pentane. These have a large vapour-pressure at ordinary temperatures, and consequently also a large scattering power, and were also found to have no tendency to form fogs or decompose under the action of light. As these vapours either act on or are absorbed by the paint used inside the cross-tube, another cross-tube of the same dimensions was used. The inside was not painted with any substance, but was merely chemically blackened. The background in this case was not of course as perfect as in the cross-tube used for the gases; but as the vapours have relatively a very large scattering power, it was thought that the background could not have introduced any appreciable error.

### *3. Preparation and Supply of Gases and Vapours.*

The gases experimented upon were oxygen, hydrogen, carbon dioxide, nitrous oxide, and air. Of these, oxygen and carbon dioxide were bought in compressed cylinders, and were nearly quite pure. As hydrogen and nitrous oxide could not be had in cylinders at Calcutta, they were prepared

in the laboratory in the usual way. Hydrogen was prepared from pure  $\text{H}_2\text{SO}_4$  and pure zinc in a Kipp's apparatus. The gas was passed in succession through potassium hydroxide and strong sulphuric acid. Nitrous oxide was prepared by heating ammonium nitrate, with the usual precautions. The gas was passed in succession through potassium hydroxide and strong sulphuric acid. During the whole time of observation the gases were passed at a slow rate so as to get always fresh gas under observation and thus avoid the formation of any fog, though there was no evidence of such formation. The cross was first exhausted, and the gas was then allowed to stream. In each case, before any observations were taken the gas was allowed to pass for a sufficiently long time to ensure that all air had been driven out. The gases were dried over phosphorus pentoxide before they entered the cross.

As the dark glass plate cemented to the bottle was not meant to stand any outward pressure, precautions had to be taken in filling the cross with the gas to see that at no time did the pressure inside exceed one atmosphere. To do this the entrance-tube was connected to a glass T-tube. Through one arm the gas was allowed to stream, and the other arm was connected to a long narrow tube dipping in mercury. Thus the pressure in the cross-tube could be registered, and at the same time, if the pressure inside exceeded one atmosphere, the gas could escape freely. As soon as the pressure was one atmosphere the manometer-tube was closed and the exit-tube opened.

In the case of vapours the cross-tube was connected to a small quantity of pure liquid and exhausted. The tube was filled with the vapour by the evaporation of the liquid.

#### 4. *Adjustments and Results.*

The cross was mounted in position and the two lenses arranged to give a beam of light parallel to the axis of the cross-tube. The adjustments could be made by observing the patches of light at the two windows. The double-image prism and the nicol were mounted in front of the observation window so as to be in the direction of the axis of the tube. The double-image prism was so adjusted that the duplicate images were just touching and in continuation of each other. The patch of light under observation was nearly rectangular, and was of fair width. As before stated, a slight error in setting the double-image prism involves only a negligible error in the measurements. To set the double-image prism accurately in position, measurements of the ratio of the intensities

were made near and on either side of the correct position of the double-image prism by altering its position slightly, and by trial the position which gave the minimum ratio was determined. This gave the correct position for the double-image prism.

Before starting the measurements, the blackness of the background was tested when the light was on by pumping out all the gas. Further, of the gases chosen, hydrogen scattered least, and showed an imperfection of polarization of less than 4 per cent. The weaker component due to hydrogen should thus be excessively feeble. It was found that even this faint track could be easily seen as a bright patch against a perfectly dark background, provided of course the eye was sufficiently accustomed to darkness. There was thus no reason to suspect that the background was defective in any way. Measurements were accordingly made with confidence. In the case of vapours, the scattered light was many times brighter than in gases, and the observations were distinctly more easy.

A large number of readings (not less than fifty) were taken for each gas, and the mean of all these was taken to calculate the ratio. The following table gives the final results.

Ratio of Weak to Strong Component in percentages.

	Authors.	Rayleigh's later results.	Rayleigh's earlier results.
H <sub>2</sub> .....	3.6 *	3.83	...
O <sub>2</sub> .....	8.4	9.4	...
CO <sub>2</sub> .....	10.6	11.7	...
Air.....	4.37	5.0	...
N <sub>2</sub> O .....	14.3	15.4	...
Benzene.....	6.8	...	6.0
Pentane.....	2.8	...	1.2
Ether.....	3.0	...	1.7

It will be seen from the above figures that the values obtained for the imperfection of polarization of gases are much higher than any of those of previous investigations except those obtained in Rayleigh's final work, and that in the case of the five gases studied, Rayleigh's final

\* It may be remarked that the imperfect polarization determined visually for H<sub>2</sub> agrees very closely with the value deduced by Havelock from dispersion theory (Proc. Roy. Soc., May, 1922, p. 164).

*Phil. Mag.* S. 6. Vol. 46. No. 273. Sept. 1923. 2 F

values are distinctly higher than ours. The cause of the discrepancy is not entirely clear. It will be noticed that Rayleigh worked with an arc lamp and by photographic photometry, whereas we used the visual region of the spectrum and direct eye observation. To determine whether a difference in the effective wave-length has an effect on the state of polarization, a series of observations were made with colour filters. The effect was carefully looked for in carbon dioxide, oxygen, and air. For getting different wave-lengths, Wratten colour filters were interposed in the path of the light, and, as before, a large number of readings were taken for each colour. It was found that throughout the visible region the polarization was practically constant, and it would seem therefore that the difference cannot be attributed to this cause. We are of opinion that the visual method is particularly direct and simple, and that the results given by it are entitled to considerable weight. In regard to the three vapours studied, Rayleigh's results obtained in his earlier work are, we think, decidedly too low.

210 Bowbazaar Street,  
Calcutta,  
March 22nd, 1923.

*XLV. The Reaction of the Air to a Circular Disk Vibrating about a Diameter. By E. T. HANSON, B.A.\**

THE following short paper was initially suggested to the author by a study of the oscillations of projectiles. It is, however, of more importance as the discussion of a hydrodynamical problem which admits of solution.

It is submitted partly as an example which bears interesting comparison with the corresponding problem solved by Lord Rayleigh in his 'Theory of Sound,' vol. ii. p. 302; partly also as an illustration of the use of Bessel's functions and the associated functions.

If a rigid body be executing small oscillations in air, it experiences two reactions. One is manifested as an increase in the inertia of the body. The other as a damping force tending to decrease the amplitude of the oscillations.

So far as I know the problem has been completely solved in two cases.

These are :—

- (1) The infinite plane wall bounded on one side by the fluid and oscillating normally to itself.
- (2) The spherical pendulum.

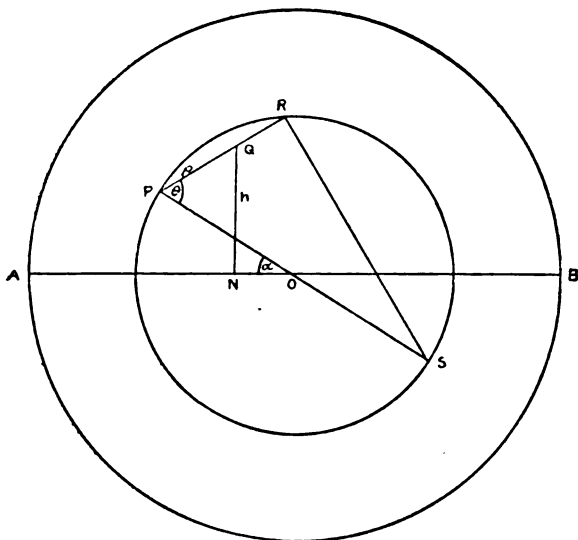
\* Communicated by the Superintendent of the Admiralty Research Laboratory. The author is indebted to the Admiralty for permission to publish this paper.

In both of these cases the forced motion at every point of the fluid can be determined.

The only other problem that has been solved is that of a circular disk vibrating normally to itself in a circular hole in an infinite plane wall. This is the problem already referred to as having been solved by Lord Rayleigh. Its solution consists of expressions for the increase in inertia and the damping force due to the reaction of the air, but no account is taken of the effect of the edge of the disk upon the motion.

In all these cases the motion is symmetrical about an axis. No solution has hitherto been given for the case of a rigid body vibrating about a fixed axis, and for this reason as well the problem is worth consideration. In this paper expressions are found for the reaction of the air to a circular disk vibrating about a diameter in a circular hole in an infinite plane wall. In this case also no account is taken of the effect of the edge of the disk, but, since this limitation is common to both problems, it is probable that the comparison is only slightly vitiated.

Fig. 1.



In fig. 1, AB is the fixed diameter about which the disk is executing small oscillations. Let  $dS_Q$  be an infinitesimal area at Q distant  $\rho$  from P. Let  $\frac{\partial}{\partial n}$  denote differentiation normally to the disk. Let  $\phi$  be the velocity potential at P

2 F 2

due to the sources brought into play by the vibration of the disk. Then

$$\phi = -\frac{1}{2\pi} \iint \frac{\partial \phi}{\partial n} \cdot \frac{e^{-ik\rho}}{\rho} dS_Q, \quad \dots \quad (1)$$

where  $\frac{2\pi}{k} = \lambda$  is the wave-length in air corresponding to the period of vibration of the disk.

We assume a time factor  $e^{i\sigma t}$  for the vibration of the disk. If  $\delta p$  denote the change of pressure at P,

$$\left. \begin{aligned} \delta p &= -\rho_0 \dot{\phi} \\ &= -i\rho_0 \sigma \phi, \end{aligned} \right\} \quad \dots \quad (2)$$

where  $\rho_0$  is the undisturbed density of the air. The change of pressure on an element of the plate at P is, therefore,

$$-i\rho_0 \sigma \phi dS_P.$$

Let the angular oscillation about AB be given by

$$\Omega = \omega e^{i\sigma t}.$$

If  $h$  be the perpendicular distance of Q from AB

$$\frac{\partial \phi}{\partial n} = h\Omega.$$

Hence

$$\phi = -\frac{1}{2\pi} \iint h\Omega \frac{e^{-ik\rho}}{\rho} dS_Q, \quad \dots \quad (3)$$

For the total turning moment reacting upon the disk we have

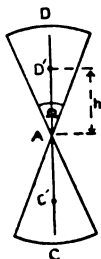
$$M = -\frac{i\rho_0 \sigma}{\Omega} \iint h\Omega \phi dS_P, \quad \dots \quad (4)$$

In order to effect the integration of (3) it is convenient to take an analogy from the theory of the ordinary potential, a method first suggested by Maxwell. Looking at the disk edgewise (fig. 2), construct a very narrow double wedge on each side of the diameter of oscillation which is perpendicular, through A, to the plane of the paper. Let  $\Omega$  be the small angle of this wedge.

Divide the face of the disk into small equal areas  $dS$ . Let  $h$  be the perpendicular distance of one of these small areas from the diameter of oscillation.

Considering the wedge as a solid body let its density be taken as unity. Then the mass of a small cylinder, whose generating lines pass through the boundary of  $dS$  and are perpendicular to  $CD$ , is  $h\Omega dS$ .

Fig. 2.



If we assume the law of attraction between two small masses to be such that their potential is proportional to  $e^{-ik\rho}/\rho$ , where  $\rho$  is the distance between them, then  $\phi$  may be said to represent the potential at any point due to the wedge.

Consider now the work that would require to be done to disintegrate the wedge and carry the fragments to infinity. Suppose that this is done ring by ring and that the portion  $DD'CC'$  has already been dissociated.

Let  $P$  be a point on the circumference of the remaining portion of the wedge, then the work expended in taking a small element to infinity is

$$\phi_P h\Omega dS,$$

where  $\phi_P$  is the potential at  $P$  due to the remaining portion of the wedge.

Hence the whole work done in disintegrating the wedge is

$$\iint \phi_P h\Omega dS. \quad \dots \quad (5)$$

If the centre portion  $C'D'$  had been first removed and if  $\phi'_P$  were the potential at  $P$  due to the remaining outer portion  $CC'DD'$ , then the whole work expended could be expressed by

$$\iint \phi'_P h\Omega dS. \quad \dots \quad (6)$$

It is evident that

$$\phi_P + \phi'_P = \phi$$

and that (5) and (6) must be equal.

Hence

$$\iint h\Omega \phi dS = 2 \iint h\Omega \phi_P dS.$$

If  $\phi$  be now written for  $\phi_P$ , (3) becomes

$$\phi = -\frac{\Omega}{\pi} \iint h \frac{e^{-ik\rho}}{\rho} dS_Q. \quad \dots \quad (7)$$

After integration of (7)  $\phi$  must be substituted in (4).

We have now to evaluate the double integral in (7). From fig. 1 we have

$$h = \rho \sin(\theta - \alpha) + c \sin \alpha. \quad \dots \quad (8)$$



Hence

$$\phi = -\frac{\Omega}{\pi} \int \int \{\rho \sin(\theta - \alpha) + c \sin \alpha\} e^{-ik\rho} d\theta d\rho, \quad (9)$$

where the integration has to be taken over the portion PRS of the disk.

Let  $z = 2kc$   
and let

$$\begin{aligned} \int_{-\frac{1}{2}\pi}^{+\frac{1}{2}\pi} e^{-iz \cos \theta} d\theta &= 2 \int_0^{+\frac{1}{2}\pi} e^{-iz \cos \theta} d\theta \\ &= 2P. \end{aligned}$$

We shall require the following results:—

$$\text{and } \left. \begin{aligned} \int_{-\frac{1}{2}\pi}^{+\frac{1}{2}\pi} \sin \theta \cos \theta e^{-iz \cos \theta} d\theta &= 0 \\ \int_{-\frac{1}{2}\pi}^{+\frac{1}{2}\pi} \sin \theta e^{-iz \cos \theta} d\theta &= 0. \end{aligned} \right\} \quad \dots \quad (10)$$

If we first integrate (9) with respect to  $\rho$  from 0 to  $2c \cos \theta$ , and use (10) we obtain

$$\begin{aligned} \phi = -\frac{\Omega}{\pi} \int_{-\frac{1}{2}\pi}^{+\frac{1}{2}\pi} \left[ -\sin \alpha \left\{ \left( \frac{i}{k^2} z \cos^2 \theta + \frac{1}{k^2} \cos \theta \right) e^{-iz \cos \theta} - \frac{1}{k^2} \cos \theta \right\} \right. \\ \left. + \sin \alpha \left\{ \frac{i}{2k^2} z e^{-iz \cos \theta} - \frac{iz}{2k^2} \right\} \right] d\theta. \quad \dots \quad (11) \end{aligned}$$

Now P satisfies the differential equation

$$\frac{\partial^2 P}{\partial z^2} + \frac{1}{z} \frac{\partial P}{\partial z} + P = -\frac{i}{z}. \quad \dots \quad (12)$$

Using (11), (12), and (4) it is not difficult to show that

$$M = -i\rho_0\sigma \int \int \frac{h\Omega}{\pi} \left[ 4i + zP + 4 \frac{\partial P}{\partial z} + z \cdot \frac{\pi}{2} \right] \frac{i \sin \alpha}{k^2} dS_P, \quad (13)$$

the integration to be taken over the whole disk.

The right hand side of (13) can be integrated with respect to  $\alpha$ , using

$$h = c \sin \alpha$$

and

$$dS_P = c d\alpha dc.$$

We then get

$$M = \frac{\rho_0 \sigma \Omega H}{8k^5}, \dots \dots \dots (14)$$

where

$$H = \int_0^{2kR} z^2 \left\{ 4i + zP + 4 \frac{\partial P}{\partial z} + z \frac{\pi}{2} \right\} dz,$$

and  $R$  is the radius of the disk.

Then with the help of (12) we can show that

$$H = \left| -z^3 \frac{\partial P}{\partial z} + 6Pz^2 - 12 \int zP \partial z + \frac{\pi z^4}{8} + iz^3 \right|_0^{2kR}. \quad (15)$$

Now

$$\left. \begin{aligned} P &= \frac{\pi}{2} [J_0(z) - i K_0(z)], \\ \text{where } K_0(z) &= \frac{2}{\pi} \int_0^{\frac{1}{2}\pi} \sin(z \sin \theta) \partial \theta. \\ \text{Also } \frac{\partial J_0}{\partial z} &= -J_1, \\ \frac{\partial K_0}{\partial z} &= \frac{2}{\pi} - \frac{K_1}{z}, \\ \int z J_0 \partial z &= z J_1, \\ \int z K_0 \partial z &= K_1. \end{aligned} \right\} \dots \dots (16)$$

$J_0$  and  $J_1$  are the Bessel functions of order zero and first respectively.

Substituting from (16) in (15) the latter can be reduced to

$$\begin{aligned} -H &= \left[ z J_1 \left\{ 6\pi - \frac{\pi}{2} z^2 \right\} - 3\pi z^2 J_0 - \frac{\pi z^4}{8} \right] \\ &\quad - i \left[ K_1 \left\{ 6\pi - \frac{\pi}{2} z^2 \right\} - 3\pi z^2 K_0 + 2z^3 \right] \\ &= A + iB, \text{ say, } \dots \dots \dots (17) \end{aligned}$$

in which the variable  $z$  now stands for  $2kR$ .

Whence

$$-M = \frac{\rho_0 \sigma \Omega}{8k^5} (A + iB). \dots \dots \dots (18)$$

$$= -A_1 \Omega - iB_1 \sigma \Omega, \text{ say. } \dots \dots (19)$$

Let  $I$  be the moment of inertia of the disk about its axis of oscillation. Let  $K$  be the oscillatory couple, of period  $2\pi/\sigma$ , applied to the disk.

Then the equation of motion of the disk is expressed by

$$(I + B_1) \frac{\partial \Omega}{\partial t} + A_1 \Omega = K. \quad (20)$$

$B_1$  therefore represents an addition to the inertia of the disk and  $A_1$  is a damping coefficient due to the expending of energy in the production of waves. Two cases are of interest, namely, when  $R$  is small compared to the wave-length and when  $R$  is correspondingly great.

The expansions of  $K_0$  and  $K_1$  are

$$\frac{\pi}{2} K_0 = z - \frac{z^3}{1^2 \cdot 3^2} + \frac{z^5}{1^2 \cdot 3^2 \cdot 5^2} - \dots,$$

$$\frac{\pi}{2} K_1 = \frac{z^3}{1^2 \cdot 3} - \frac{z^5}{1^2 \cdot 3^2 \cdot 5} + \frac{z^7}{1^2 \cdot 3^2 \cdot 5^2 \cdot 7} - \dots$$

When  $z$  is small,

$$\left. \begin{aligned} A &= -\frac{\pi z^8}{2 \cdot 2 \cdot 4 \cdot 4 \cdot 6 \cdot 8}, \\ B &= -\frac{z^5}{1 \cdot 3 \cdot 5}. \end{aligned} \right\} \quad (21)$$

Considering first the addition to the inertia, we have

$$B_1 = \frac{4\rho_0 R^5}{1 \cdot 3 \cdot 5},$$

so that  $B_1$  is independent of the period and the wave-length.

Imagine a hemisphere of air to become rigid on one side of the disk, and to oscillate with the disk.

The moment of inertia of this hemisphere about the diameter of oscillation is  $\pi B_1$ .

Hence the increase of inertia is represented by  $1/\pi$  times the inertia of such a hemisphere.

The damping term is observed to be extremely small, a result which is to be expected in the absence of viscosity, but its magnitude has not been hitherto determined.

In the case of the disk oscillating normally to itself the damping term is proportional to  $R^4$ .

When  $z$  is large we require the asymptotic expansions of  $J_0 J_1 K_0 K_1$ .

The first terms in the expansions are

$$J_0 = \left(\frac{2}{\pi z}\right)^{\frac{1}{2}} \cos\left(z - \frac{\pi}{4}\right), \quad J_1 = -\left(\frac{2}{\pi z}\right)^{\frac{1}{2}} \sin\left(z - \frac{\pi}{4}\right),$$

$$K_0 = \left(\frac{2}{\pi z}\right)^{\frac{1}{2}} \sin\left(z - \frac{\pi}{4}\right), \quad K_1 = \frac{2z}{\pi}.$$

Hence when  $z$  is large

$$\left. \begin{aligned} A &= -\frac{\pi z^4}{8}, \\ B &= -z^3. \end{aligned} \right\} \dots \dots \dots (22)$$

The above solution is interesting as compared with that for the disk oscillating normally to itself. The great difference between the two solutions is due to the fact that, in the problem just solved, the air on opposite sides of the diameter of oscillation is in opposite phases of its motion.

For small values of  $z$  the series  $K_0$  and  $K_1$  are both rapidly convergent. Even when  $z=2$  only four terms of each series are required to obtain values correct to three decimal places.

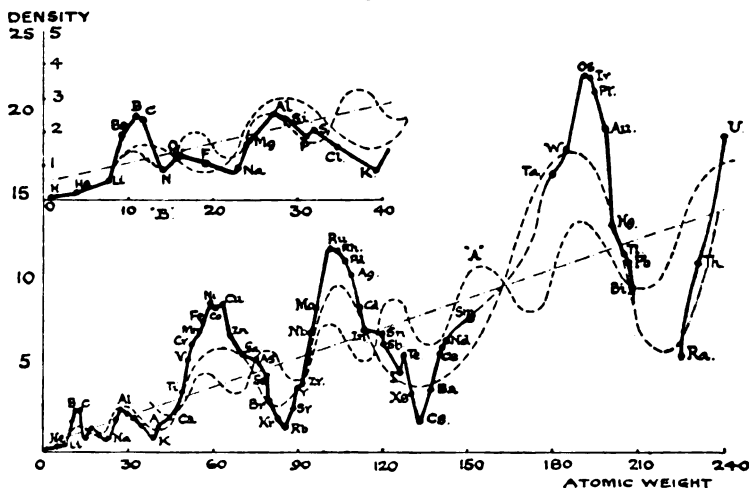
The following short table may be found useful :—

$z$ .	$\frac{\pi}{2} K_0$ .	$\frac{\pi}{2} K_1$ .
0	0	0
·2 .....	·119	·003
·4 .....	·393	·021
·6 .....	·576	·072
·8 .....	·745	·164
1 .....	·893	·311
1·2 .....	1·019	·523
1·4 .....	1·125	·782
1·6 .....	1·189	1·149
1·8 .....	1·230	1·561
2 .....	1·243	2·031

XLVI. *The Curves of the Periodic Law.*—II. By W. M. THORNTON, *Professor of Electrical Engineering in Armstrong College, Newcastle-on-Tyne* \*.

1. **T**HE rise and fall of the densities of the elements shown in fig. 1 resembles the side elevation of a somewhat irregular spiral drawn upon a transparent cone. The end elevation of such a curve of uniform angular pitch is a logarithmic spiral. This possibly suggested the scheme of representation of the elements on such a spiral given by Dr. Johnstone Stoney, in which the densities of the argon group were forecast †. Sir William Crookes, in his Presidential Address to the Chemical Section of the British Association in 1886, arranged the elements symmetrically about a line through those of maximum density, and obtained a zigzag curve dividing the elements in a remarkable manner. The present note deals with the minor fluctuations of the density curve.

Fig. 1.



The periods of the oscillations in fig. 1 increase with distance from the origin, but not so uniformly as they do on the cone spiral, where they are strictly proportional to it. Any regular periodic curve of this kind can be represented by a combination of harmonic curves chosen by inspection or analysis. The larger dotted curve in fig. 1 is that which

\* Communicated by the Author.

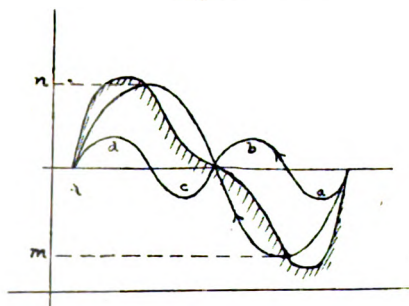
† Phil. Mag. [6] iv. pp. 411, 504 (1902).

appears to fit the observed curve of densities best as a fundamental, amplitude and period varying. It is the representation of that great periodic change in the configuration of the outer electrons in an atom under their own forces which a successful theory of atomic formation must explain. It is not the graph of the central force of the nucleus, for this, being proportional to the nuclear mass, changes by uniform steps, and is represented by the dotted straight centre line.

On the fundamental curve there is superposed one of double frequency, the amplitude and phase of which in fig. 1 are chosen by inspection. This curve can be regarded by analogy as representing some form of retardation in the change of atomic volume of the nature of hysteresis\*—that is, a change of arrangement caused by the resultant force to which the fundamental is due, always occurring so as to produce the same deviation from the mean position in successive half periods.

In fig. 2, moving from right to left, the effect of the

Fig. 2.



double period at *a* is to make the resultant density less than normal, taking the fundamental curve to represent the normal type of change. At *b* it is greater, at *c* less, and at *d* greater.

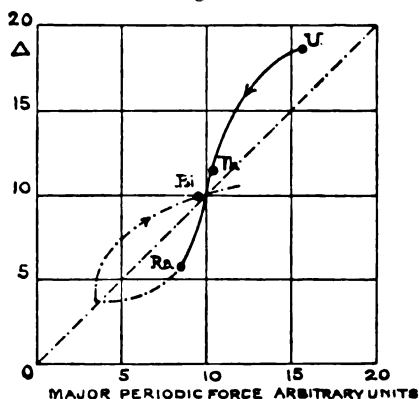
2. The physical and chemical properties of the elements appear to depend as much upon the minor periodic change as upon the fundamental. In order to bring out the differences between them, curves are given below in which the ordinates are densities, and abscissæ the projections of the major harmonic curve on the vertical axis. Thus in fig. 5, to take a clear example, the horizontal range from 3 to 11.5 arbitrary units corresponds to *mn* on the vertical axis of fig. 2, where

\* Phil. Mag. xxxiv. pp. 70-75 (July 1917).

this represents the oscillations of the fundamental in that part of the curve of densities. The abscissæ being drawn to the same scale as the densities, the centre line of the loops is inclined at 45 degrees. If the density rose and fell in every case proportionally to the fundamental alone the loops would close on to the centre line.

The first curve (fig. 3) contains uranium, thorium, and radium. Of these, the first two have densities greater than normal, as shown by the position of the minor periodic curve drawn above the mean line in fig. 1. Radium is somewhat below it. Densities greater than normal in reference to the major periodic curve may be called *over-saturated*; radium is, on this view, *under-saturated*.

Fig. 3.



The second group (fig. 4) begins with bismuth and ends with cesium, passing through the region of rare earths. This loop differs from the rest in having double flexure on the descending side. The elements there are alternately *over-* and *under-saturated* twice in falling from the maximum to the minimum. This appears to have had a marked influence on the densities of the rare elements. Those whose densities are known—erbium 4·7, lanthanum 6·1, praseodymium 6·47, cerium 6·68, neodymium 6·95, samarium 7·75—all lie on a small part of the curve in the neighbourhood of cerium. It would seem that, after tantalum, the elements which should lie immediately below it in fig. 4 are unable to form in the usual manner, and precipitate into a group having normal atomic weights, so that they take their places in the descending scale of elements, but abnormally small densities.

3. For the electric degradation theory of matter to be consistent, the increasing radioactivity from uranium to radium should be capable of explanation as a consequence of

Fig. 4.

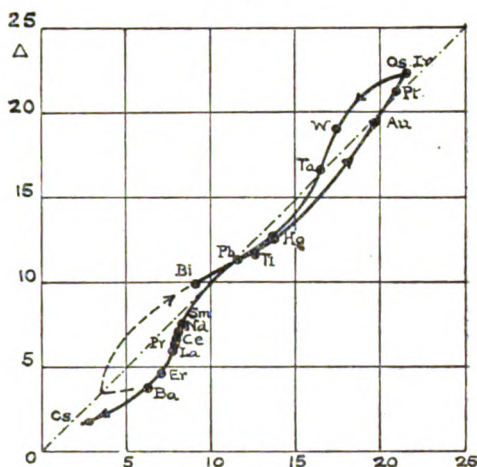
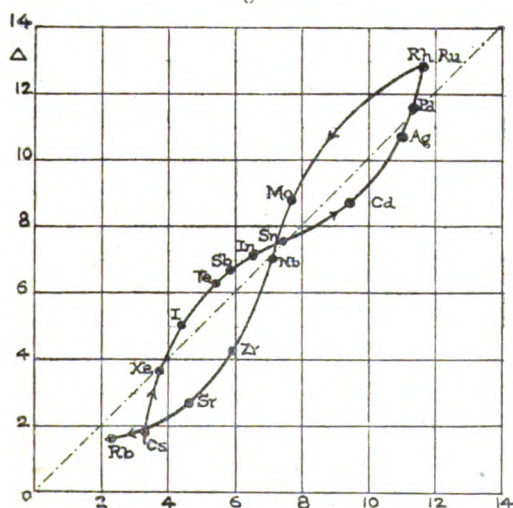


Fig. 5.



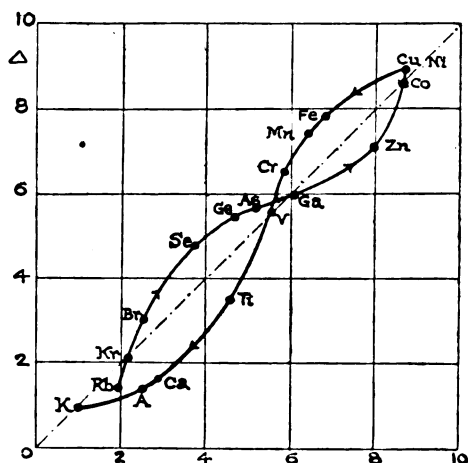
feeblor control or of stronger force of expulsion. If the rate of change of density with atomic weight were such that the loss of the smallest possible unit of mass produced very



great expansion of the remaining electric structure, the atom would be on the point of explosion, and any increase in the rate would make it impossible for an atom to cohere.

When an atom is already relatively light, a rapid fall of the curves of figs. 3 to 8 usually means instability, as in radium, or perhaps scarcity, as in the rare earths. In figs. 7 and 8 there are no elements in that part of the curve. When, on the other hand, the atoms are contracting and their density increasing, the first steady atom to be formed, that is bismuth, implies the cessation of instability, and it is not normally radioactive.

Fig. 6.

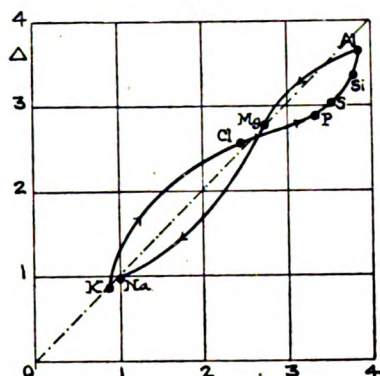


The increase of density from bismuth to osmium in fig. 1 is extremely rapid, and the maximum is reached more to the right of the main period maximum than in the other cases. In falling from this maximum, the force is aided by the falling minor period, and is constrained to pass to the right rather than to the left of the crest at A. One possible cause of the rare earths may be contained in the reason for the very rapid shrinkage of the atomic structure from bismuth to osmium, and any theory of atomic formation by grouping of electrons should account for strong forces of contraction in this region.

There are more elements on the side of the curve in which the density is rising as the atomic weight falls, than on the descending side—that is, atoms shrink slowly and expand quickly with fall of atomic weight.

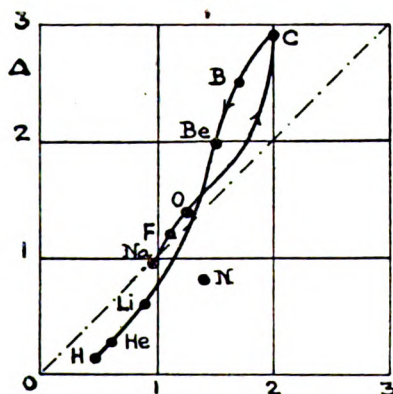
In general, elements on the rising side of the upper loop, such as gold or silver, are relatively under-saturated and ductile, while those on the falling side are harder. The same characteristic properties are in figs. 6 and 7.

Fig. 7.



As might be expected, the positions on the curves indicate with few exceptions their corresponding places in the tables of the periodic law. The density of liquid nitrogen, however, follows not the main period, but the minor, as seen in fig. 1 at B, and it is half as dense as it would have been had it

Fig. 8.



followed the curve of fig. 8 after oxygen. It will be noted that there are no elements even in fig. 6 at the tops of the curves on the over-saturated, *i. e.* falling side, and there are none in fig. 7 above the centre line of mean density.

4. This mode of representing densities in reference to a smooth harmonic curve of the same period as the observed curve of fig. 1 is not speculative, for, after the cause of spectra and valency, the existence of a periodic centripetal force or resultant pressure is the most evident fact an electric theory of atomic formation has yet fully to explain. It can hardly be doubted that the double period oscillation of the density curve indicates the presence of an important factor in atomic formation. This can only arise in the adjustments of the positions of the outer electrons with each loss of a proton from the nucleus. It is premature to speculate on its nature, but since the main rise and fall of density indicate successive storage and release of potential energy in the atom, the double period curve indicates where this is retarded or increased. The effect is common to hysteresis in any cyclic operation, magnetization of iron for example, in which change is at first retarded and later accelerated by intermolecular forces. In the present case it is possibly a consequence of the limitations of position entailed by the restricted number of electrons. The existence of elements with widely different properties seems to depend upon having comparatively few electrons in the rings. If there were many more the number of positions of stability would be increased and characteristic differences lessened.

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*XLVII. Note on the Illumination of the Spectroscope with End-on Vacuum Tubes. By T. R. MERTON, F.R.S., and R. C. JOHNSON, B.A., B.Sc.\**

[Plate IX.]

ONE of the essential conditions in the accurate determination of wave-lengths by micrometric measurements of spectra which are photographed in juxtaposition, consists in securing that the prism or grating shall be uniformly and completely illuminated both in the case of the comparison spectrum and the spectrum under investigation. The difficulty of securing this is greatly aggravated when vacuum tubes are used as a source of light in an end-on position; and it can at once be seen that it is, in fact, impossible to illuminate the prism or grating quite uniformly under these conditions unless the aperture of the spectroscope is very small, since the pencil of rays which emerge axially from the capillary subtend a very small angle, and result in the formation of a bright spot on the collimating lens. Prof. Fowler has informed us that this fact may be largely

\* Communicated by the Authors.

responsible for the difficulty which is always experienced in getting reliable wave-length measurements from end-on tubes. It has been found that a considerable advantage can be gained both as regards the evenness of illumination and the total intensity by silvering, by the usual chemical methods, the outer walls of the capillary. It is obvious that this must be the case, but the exact theoretical investigation is rather complicated and tedious. To test the question experimentally a vacuum tube of the usual H form with a capillary about 2 mm. internal bore and 25 cm. long was prepared, the capillary being bent in the centre through about a right angle. The tube contained air at a few millimetres pressure, and one half of the capillary was silvered externally. A qualitative comparison of the intensity from the two ends was then made as follows.

The tube was excited by means of an alternating current transformer, and photographs with the same time of exposure were taken of each end of the capillary in an end-on position, using an ordinary photographic camera arranged to bring the end of the capillary to a focus about halfway between the camera lens and the photographic plate. The pattern on the plate was thus similar to that which would be formed on the collimating lens of a spectroscope with a condensing lens between the vacuum tube and the slit. The patterns from the two ends of the capillary were photographed in adjacent positions on the same plate, and a typical result is shown in Pl. IX., where A is the extra-focal image from the unsilvered, and B that of the silvered capillary.

The gain in intensity and uniformity in B is plainly seen, as also the rings surrounding the bright spot due to the axial pencil of rays. This peculiar system of rings is due to reflexions from the inner walls of the capillary, and can be seen, for example, when light from an extended source is viewed through a polished cylindrical tube. It is seen that with end-on tubes certain zones of the dispersing system are more effectively illuminated; and these only receive a small fraction of the light in comparison with the central spot due to the axial pencil. With a silvered capillary this effect is greatly mitigated, but it is clear that with the unsilvered tube there is not only a serious source of error if the tube is not very carefully adjusted but a very appreciable reduction in the resolving power of the spectroscope.

The Clarendon Laboratory,  
Oxford,  
March 7th, 1923.

XLVIII. *Unit Magnification Surfaces of a Glass Ball.*  
 By ALICE EVERETT, M.A., *National Physical Laboratory* \*.

THE theory of the unit surfaces of lenses may be regarded as the generalization of the theory of the unit or principal planes which play so large a part in elementary lens design. The unit surfaces are the loci traced by pairs of conjugate points for unit magnification on rays bound by some condition, such as passing through a fixed point O. There are two separate problems to consider according as the conjugate points are the primary or secondary foci of each other. In either case it has been found that the positions and forms of the loci change with the position of the fixed point. For a symmetric system the unit surfaces, both primary and secondary, for any position of O on the optic axis all touch the Gaussian unit or principal planes at their points of intersection with the axis, the equations of the principal planes being merely a first approximation to the equations of the unit surfaces, on the assumption that the inclinations and incident heights of the rays are so small that their squares are negligible.

The case of rays from a fixed point O incident upon a solid glass sphere in air will serve as a simple illustration.

Magnification at a point is generally different in different directions. In the present case, unit magnification is taken to signify equality of conjugate line elements drawn perpendicular to the ray, and lying in the meridional plane, or in the sagittal planes through the ray, according as we are dealing with the primary or secondary foci, respectively.

First it will be shown that for a single ray refracted through a sphere, the secondary unit points coincide at the point of intersection of the incident and emergent paths, and the primary unit points are the feet of the perpendiculars from the centre upon the incident and emergent paths.

Let C be the centre of the sphere (fig. 1); O the fixed point; A and B the points of incidence and emergence; M the middle point of AB; S the point of intersection of the incident and emergent rays AS, SB; and P and P' the feet of the perpendiculars from C upon these rays. S obviously lies on CM. The whole path of the ray lies in the diametral plane ACB, and is symmetrical with respect to the diameter CM.

Hence the images of M formed at the two faces of the

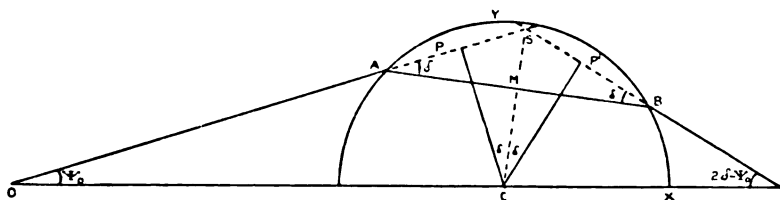
\* Communicated by the Author.

sphere by thin pencils proceeding outwards from  $M$  along  $MA$ ,  $MB$  will be equal, and therefore the points conjugate to  $M$  with respect to the two faces will be a pair of unit points with respect to the whole sphere.

It is known that for a single refraction the secondary foci lie on a straight line through the centre. Thus the point  $S$  is the secondary focus of  $M$  for either face of the sphere, and therefore the secondary unit points for the whole sphere coincide at  $S$ , which is a self-conjugate point.

As regards the primary foci, it is known that in the case of a single surface the feet of the perpendiculars from the centre of curvature on the incident and refracted rays are conjugate points. Therefore  $P$  is the primary focus of  $M$

Fig. 1.



Refraction through a Glass Ball (Solid Sphere).

for refraction at the first face, and  $P'$  is the primary focus of  $M$  for refraction at the second face. Hence  $P$ ,  $P'$  are primary unit points.

The positions of the unit points may be verified by putting the magnification equal to unity in the known formulæ connecting focal distance and magnification.

The above reasoning may evidently be extended to the case of symmetrical refraction through  $n$  concentric spheres bounding homogeneous media, or ( $n = \infty$ ) a single sphere with density a function of distance from the centre.

The next step is to find the loci of the unit points for rays through  $O$  in a plane through  $OC$ . The unit surfaces are evidently the surfaces of revolution generated by rotating these plane loci about  $OC$ .

The Gaussian unit planes coincide in the plane through  $C$  at right angles to  $OC$ . The plane loci of  $P$  and  $P'$  are evidently the pedal curves of the caustics, or envelopes, of the incident and emergent rays respectively.

The plane locus of  $P$ , the object primary unit point, is obviously a portion of a semicircle on  $OC$  as diameter. The

loci of P' and S are curves of higher degree, though the graphic construction is so simple and evident that description is needless.

Let  $\phi, \phi'$  be the angles of incidence and refraction at the first face of the sphere;  $\psi$  the inclination of the incident ray to OC;  $\delta = \phi - \phi'$ ;  $r$  = radius; and  $c = OC$ .

Then  $\sin \phi = \mu \sin \phi'$ , and  $r \sin \phi = c \sin \psi$ .

Taking C, the centre of the sphere, as origin of coordinates, and OC as axis of  $x$ , the following are the polar coordinates of the points named:—

$$\begin{array}{ll} \text{S} & \rho = r \sin \phi \sec \delta, \quad \theta = 90^\circ - (\delta - \psi), \\ \text{P}' & \rho = r \sin \phi, \quad \theta = 90^\circ - (2\delta - \psi), \\ \text{M} & \rho = r \sin \phi', \quad \theta = 90^\circ - (\delta - \psi). \end{array}$$

The Cartesian coordinates are:—

$$\begin{array}{ll} \text{S} & x = r \sin \phi \sec \delta \sin (\delta - \psi), \quad y = r \sin \phi \sec \delta \cos (\delta - \psi), \\ \text{P}' & x = r \sin \phi \sin (2\delta - \psi), \quad y = r \sin \phi \cos (2\delta - \psi), \\ \text{M} & x = r \sin \phi' \sin (\delta - \psi), \quad y = r \sin \phi' \cos (\delta - \psi). \end{array}$$

It can easily be seen from the above that all the loci touch the axis of  $y$  at the centre of the sphere. Also, by finding  $dy/dx$ , it can be shown that for  $\phi = 90^\circ$ , or grazing incidence (which by symmetry involves grazing emergence), the locus of S touches the incident path at its point of intersection with a circle concentric with the given circle, and of radius  $\mu r$  (the outer circle in Young's well-known construction); the locus of P' touches the refracting circle and the emergent ray at their point of contact; and the locus of M touches the path in the sphere at its point of intersection with a concentric circle of radius  $r/\mu$  (Young's inner circle).

In the case where O lies at infinity and the incident rays are parallel to OC, the following comparatively simple polar equations are found for the plane unit loci, the axis of  $y$  being taken as initial line, and  $\chi$  being the angle swept out by the radius vector in the clockwise direction:—

$$\text{Locus of S} \quad \rho = \frac{\mu r \tan \chi}{\sqrt{\mu^2 + 1 - 2\mu \cos \chi}}.$$

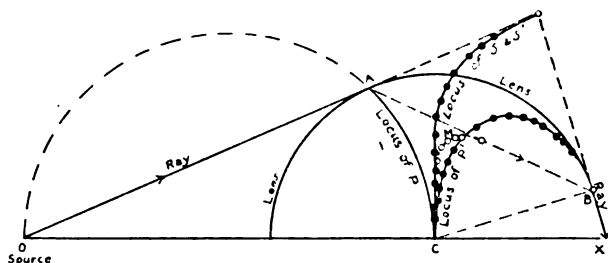
$$\text{Locus of P}' \quad \rho = \frac{\mu r \sin \frac{\chi}{2}}{\sqrt{\mu^2 + 1 - 2\mu \cos \frac{\chi}{2}}}.$$

$$\text{Locus of M} \quad \rho = \frac{r \sin \chi}{\sqrt{\mu^2 + 1 - 2\mu \cos \chi}}.$$

The denominators are equal,  $=\epsilon$  say, since the  $\chi$  of  $P'$  is double the  $\chi$  of  $S$  and  $M$ . The quantity  $r\epsilon$  is the intercept on the incident ray between the concentric circles of radii  $r$  and  $\mu r$ , while  $r\epsilon/\mu$  is the intercept on  $AB$  between the concentric circles of radii  $r$  and  $r/\mu$ .

Fig. 2 shows the axial half-sections of the unit surfaces for chief rays diverging from a point  $O$  at a distance from the centre of the sphere equal to 2.5 times the radius, when the refractive index of the glass is 1.5. As remarked above, the unit surfaces are the surfaces of revolution generated by rotating these half-sections about the axis  $OC$ . The half-section of the locus of  $M$ , which is not a unit-surface, is also shown. The loci show pronounced astigmatism and curvature. When  $\phi=0$ , they all touch the axis of  $y$  at the

Fig. 2.

Unit Surfaces of a Solid Sphere. Axial Section.  $\mu=1.5$ .

centre of the sphere. As  $\phi$  increases, the primary unit loci curve away rapidly in opposite directions, the image locus curving more rapidly than the object locus and becoming concave towards the centre in the latter part of its course. The self-conjugate secondary unit locus follows an intermediate course. The figure clearly illustrates the above theoretical deductions that at the points corresponding to grazing incidence ( $\phi=90^\circ$ ) the secondary locus touches the incident-ray path, and the image primary locus touches the refracting circle and the emergent ray at their point of contact.

If the final point of emergence, corresponding to grazing incidence, were made to fall on the point  $X$  where the axis of  $x$  cuts the sphere, by changing the position of  $O$  or the refractive index or both, then the complete plane locus of  $P'$  would become a closed curve, and the image unit surface roughly resemble an ellipsoid, though slightly lob-sided.



The case where the incident rays are parallel, and  $\mu = \sec 45^\circ = 1.4142$ , may be cited as an example.

The loci are of a stable nature. Curves drawn for other values of  $OC$  between  $\infty$  and  $1.5$  show the same general character as those in fig. 2. When  $O$  lies at infinity, the locus of  $P$  coincides with the radius along the axis of  $y$ —i. e., with the trace of the coincident Gaussian unit planes—and the point of grazing emergence or terminal point of the locus of  $P'$  lies below the axis of  $x$ , so that the emergent ray is deviated through more than a right angle, and the sphere acts like a reflector. As  $O$  moves in from infinity along the axis of  $x$  towards the refracting circle, the terminal point of the  $P'$  curve moves upwards anti-clockwise along the circumference.

For a value of  $OC$  about  $1.5$ , the  $P'$  curve begins to cross the axis of  $y$  and show a point of inflexion, and as  $O$  draws still nearer to the circumference of the circle, the curve encroaches more and more on the second quadrant. When  $O$  lies inside the circle, grazing incidence of course cannot occur.

*XLIX. On the Propagation of certain Types of Electromagnetic Waves. By D. R. HARTREE, B.A., St. John's College, Cambridge\*.*

§ 1. Introduction.

THE investigation which led to the solutions of Maxwell's equations given in the present paper was suggested originally by the properties of the disturbance in the less dense medium in the case of total reflexion at the surface of separation of two transparent media.

This disturbance of course satisfies Maxwell's equations. It is propagated without change of form as a plane wave, but its properties differ from those of the simplest type of plane wave in three respects, viz. :—

- (a) The amplitude is not constant over a wave front (defined as a continuous surface joining points of equal phase);
- (b) the wave is not purely transverse;
- (c) the wave does not travel with the normal velocity of light in the medium.

In a discussion, the question arose as to how far the

\* Communicated by Dr. T. J. 'a. Bromwich, F.R.S., Prælector in Mathematics at St. John's College, Cambridge.

existence in free æther of waves with properties (a) and (b) depended on the existence of a material boundary (which of course exists in the total reflexion case), which might be considered as a kind of support to the wave; and specially whether it was possible for a plane wave, concentrated, so to speak, in a small part of the wave front, to travel in free æther without spreading or changing its form.

## § 2. Equations of the Electromagnetic Field.

For the purposes of the present paper we need only consider the divergence equation and the wave equation for the electric intensity  $\mathbf{E}$  in free æther, viz.,

$$\text{div } \mathbf{E} = 0, \quad . . . . (2.1)$$

$$\left( \nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \right) \mathbf{E} = 0. \quad . . . . (2.2)$$

Only plane waves will be considered, and the axis of  $z$  will be taken perpendicular to the wave front.

In Cartesians, (2.1) gives

$$\frac{\partial E_x}{\partial x} + \frac{\partial E_y}{\partial y} + \frac{\partial E_z}{\partial z} = 0, \quad . . . . (2.3)$$

from which it appears that unless the amplitude varies over the wave front in such a way that

$$\frac{\partial E_x}{\partial x} + \frac{\partial E_y}{\partial y} = 0$$

a longitudinal component of  $\mathbf{E}$  must be present. When such a component is present, "plane-polarized waves" will be taken to mean waves in which the component of  $\mathbf{E}$  in the plane of the wave front has a fixed direction.

If a solution of the wave equation has the form

$$\phi(x, y) \cdot \psi(z, t),$$

then

$$\frac{1}{\phi} \left[ \frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} \right] = - \frac{1}{\psi} \left[ \frac{\partial^2 \psi}{\partial z^2} - \frac{1}{c^2} \frac{\partial^2 \psi}{\partial t^2} \right]. \quad . . (2.4)$$

The left- and right-hand sides of this equation are respectively functions of  $(x, y)$  and  $(z, t)$ , and must therefore both be constant. The simplest group of solutions is that for which this constant is zero; one solution of this group has been treated by Lord Rayleigh\* in connexion with the

\* Phil. Mag. [5] vol. xlv. p. 199 (1897); 'Scientific Papers,' vol. iv. p. 327.

propagation of electric waves along parallel cylinders. If this constant is not taken as zero, then another group of solutions is obtained. Special solutions of these two types are considered in §§ 3 and 4.

The boundary conditions for the solutions in which we are interested are  $E=0$ ,  $H=0$  at infinity in the plane of the wave front.

### § 3. Plane-polarized waves propagated with velocity $c$ .

There is no restriction in taking the axis of  $x$  in the direction of the transverse component of  $E$ .

For waves propagated with velocity  $c$

$$\frac{\partial^2 \psi}{\partial z^2} - \frac{1}{c^2} \frac{\partial^2 \psi}{\partial t^2} = 0,$$

so from (2.4) the following expressions,

$$\left. \begin{aligned} E_x &= \xi(x, y) \cdot \cos \kappa(z - ct), \\ E_y &= 0, \\ E_z &= \zeta(x, y) \cdot [a \cos \kappa(z - ct) + \sin \kappa(z - ct)], \end{aligned} \right\} \quad (3.1)$$

satisfy the wave equation if

$$\frac{\partial^2 \xi}{\partial x^2} + \frac{\partial^2 \xi}{\partial y^2} = 0, \quad \text{and} \quad \frac{\partial^2 \zeta}{\partial x^2} + \frac{\partial^2 \zeta}{\partial y^2} = 0. \quad (3.2)$$

This solution represents a wave, of wave-length  $2\pi/\kappa$ , with amplitudes varying over the wave front in the manner defined by  $\xi$  and  $\zeta$  respectively, travelling with velocity  $c$  along the axis of  $z$  without change of form.

On substituting (3.1) in the divergence equation and equating coefficients of the sine and cosine terms separately (since the divergence equation must hold for all values of  $z$  and  $t$ ), we find

$$a = 0; \quad \frac{\partial \xi}{\partial x} + \kappa \zeta = 0. \quad (3.3)$$

Obviously if  $\xi$  satisfies (3.2), then  $\zeta$  determined from (3.4) satisfies (3.2) automatically, so the divergence equation can be considered as defining  $\zeta$  when a function  $\xi$  is found satisfying the wave equation. This is also the case with the more elaborate solution considered in the next section. It will also be noticed that the condition  $a=0$  means that the

longitudinal component is in quadrature with the transverse component.

From (3.2) it follows that if  $\xi, \zeta$  are zero at infinity in all directions in the plane of the wave front, or at any boundary, then they are zero all over the wave front. Hence it is not possible for a simple plane wave with amplitude varying over the wave front to travel with the normal velocity of light unless supported in a way which makes it possible for  $\xi$  to be non-zero over some boundary, which may be internal or external to the region occupied by the wave.

§ 4. *Plane-polarized waves propagated with velocity other than  $c$ .*

The character of the wave in the less dense medium in total reflexion suggests the trial of a solution of the form

$$\left. \begin{aligned} E_x &= \xi(x, y) \cdot \cos \kappa_1(z - c_1 t), \\ E_y &= 0, \\ E_z &= \zeta(x, y) \cdot [a \cos \kappa_1(z - c_1 t) + \sin \kappa_1(z - c_1 t)], \end{aligned} \right\} \quad (4.1)$$

where

$$\kappa_1 = 2\pi\mu/\lambda = \kappa\mu, \quad \mu = c/c_1,$$

$c_1$  being the velocity of the waves considered, and  $\lambda/\mu$  their wave-length.  $\mu$  may be considered as the refractive index of the æther for the waves; for the total reflexion case it is greater than 1, and varies with the angle of incidence of the light in the denser medium. [The argument of the periodic term has been written  $\kappa_1(z - c_1 t)$  and not  $\kappa(z - c_1 t)$ , so that in the total reflexion case  $\lambda$  is the *normal* wave-length in *vacuo*.]

In these formulæ the function  $\psi(z, t)$  of (2.4) has the form

$$\psi = A \cos \kappa_1(z - c_1 t + \alpha),$$

so that

$$\frac{\partial^2 \psi}{\partial z^2} - \frac{1}{c^2} \frac{\partial^2 \psi}{\partial t^2} = -\kappa_1^2 [1 - (c_1/c)^2] \psi = -\kappa^2 (\mu^2 - 1) \psi.$$

Hence in accordance with (2.4)

$$\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} - \kappa^2 (\mu^2 - 1) \phi = 0, \quad . \quad . \quad . \quad (4.2)$$

where  $\phi$  is either of the two functions  $\xi$  and  $\zeta$ . The divergence equation gives

$$a = 0; \quad \frac{\partial \xi}{\partial x} + \kappa_1 \zeta = 0, \quad . \quad . \quad . \quad . \quad (4.3)$$

which corresponds to (3.3).

In order that  $\xi, \zeta$  shall tend to zero as  $x, y$  tend to infinity, it must be possible for a maximum value of  $\phi$  to occur when  $\phi$  has a positive value. But for  $\phi$  to be a maximum,

$$\frac{\partial^2 \phi}{\partial x^2} + \frac{\partial^2 \phi}{\partial y^2} < 0.$$

Hence from (4.2)

$$\kappa^2(\mu^2 - 1)\phi < 0,$$

so for this maximum to occur for  $\phi > 0$ ,  $\mu$  must be less than 1.

Hence if it is possible to have waves of the type required, they will be propagated with a velocity greater than the normal velocity of light.

In the case of the wave in the less dense medium in total reflexion the variation of amplitude in a direction perpendicular to the bounding surface is exponential, and its velocity is less than the normal for that medium. From this it might be expected that it would not be possible for a wave travelling with velocity less than  $c$  in free æther to satisfy the boundary conditions of zero amplitude at infinity in the plane of the wave front.

Transforming (4.2) to polars in the plane of the wave front gives

$$\left[ \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \theta^2} + \kappa^2(1 - \mu^2) \right] \phi = 0. \quad (4.4)$$

Consider the solution in which the distribution of values of  $\xi$  is such that  $\xi$  is independent of  $\theta$ . Then (4.4) reduces to

$$\left[ \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \kappa^2(1 - \mu^2) \right] \xi = 0,$$

of which the solution remaining finite at  $r=0$  is

$$\xi = A J_0[\kappa r(1 - \mu^2)^{\frac{1}{2}}]. \quad (4.5)$$

(Negative values must of course be interpreted as indicating a change of phase of  $\pi$ .) This solution satisfies the condition  $\xi \rightarrow 0$  as  $r \rightarrow \infty$ .

It appears then that the plane wave with amplitude varying over the wave front in accordance with (4.5) will be propagated without change of form with velocity  $c_1 = c/\mu$ . Since the principal maximum of  $J_0$  is more than three times as large as any other, this wave can reasonably be said to be concentrated over a small part of the wave front as compared with a simple plane wave. But since for large values of  $r$   $J_0$  is of order  $r^{-\frac{1}{2}}$ , the energy density is of order  $r^{-1}$ , and so the energy of that part of the wave contained between two

planes  $z - c_1 t = \text{constant}$  is of the order of  $r$  and so does not converge, though of course it does not diverge so rapidly as for a wave with constant amplitude over the wave front, for which the energy is of the order of  $r^2$ .

If the scale of the variation of amplitude is fixed (say by fixing the value of  $r$  for which the first zero of  $\xi$  occurs), then we must have

$$(1 - \mu^2)/\lambda^2 = \text{const.};$$

whence it follows that  $\mu$  varies with  $\lambda$ : that is to say, dispersion of light occurs *in vacuo*. It is to be emphasized that this dispersion by free æther occurs in the case of a *plane wave travelling without change of form*, and does not appear to be comparable either with the dispersion which may occur in the neighbourhood of the focus of a spherical wave\*, or with the lateral dispersion of light on which a variation of amplitude over the wave front has been impressed by a diffraction grating, for in this case there is change of form and loss of energy laterally.

The value of  $\xi$  can be found from (4.3), and the complete expression for  $E$  found to be

$$\left. \begin{aligned} E_x &= A J_0[\kappa r(1 - \mu^2)^{\frac{1}{2}}] \cdot \cos \kappa_1(z - c_1 t), \\ E_y &= 0, \\ E_z &= A[(1 - \mu^2)/\mu^2]^{\frac{1}{2}} \cdot \cos \theta \cdot J_1[\kappa r(1 - \mu^2)^{\frac{1}{2}}] \cdot \sin \kappa_1(z - c_1 t). \end{aligned} \right\} \dots (4.6)$$

The presence of the factor  $\cos \theta$  in  $E_z$  shows that the values of the longitudinal component are not symmetrical about the axis of  $z$ .

The formulæ for the components of  $H$  are rather heavy and not particularly interesting in themselves; if they are obtained and the Poynting energy vector calculated, it is found that the instantaneous value of this vector has a component in the plane of the wave front, but the value at a point integrated over a period is perpendicular to the wave front.

The solutions of (4.4), in which  $\xi$  varies with  $\theta$  as well as with  $r$ , introduce Bessel functions of order greater than zero, and are zero on the axis of  $z$  instead of having a maximum there. For large values of  $r$ , the energy integrated over the wave front is of order  $r$  as in the solution already considered.

\* See Gouy, "Sur la Propagation Anomale des Ondes," *Annales de Chimie et de Physique*, 6th ser. vol. xxiv. p. 145 (1891).

These results show that the propagation of electromagnetic waves concentrated, to a certain extent, in a small region of the wave front, without loss of energy laterally, is not inconsistent with Maxwell's equations. The possible bearing of this on the quantum theory, and particularly on the photoelectric effect, was kept in mind, and in fact partly suggested the work, but in view of the fact that the energy integrated over a wave front does not converge, it does not seem likely that the present results have any bearing on these questions.

#### § 5. *Possible experimental verification of the solution.*

It might be interesting to obtain experimental verification of the solution obtained in the last section. The properties of the waves suggest two possible experiments.

Suppose an instrument, similar to a zone plate, were constructed so as to give the variation of amplitude over the transmitted wave front required by (4.5). Then

- (1) since the waves travel unchanged once they are produced, this plate should throw a sharp shadow if placed in parallel light, without any light being diffracted, however small its scale,
- (2) the abnormal wave velocity might be detected by an interference method.

#### § 6. *Summary.*

Some solutions of Maxwell's equations are found which represent plane waves, with amplitude varying over the wave front, travelling without change of form. In general, the electric intensity in such waves will have a longitudinal component. If the waves travel with the normal velocity of light, they must be supported by some material boundary; but it is possible to find solutions representing such waves, travelling in free æther with a velocity greater than the normal velocity of light, for which the amplitude over a wave front infinite in extent is always finite. For one such solution there is a region of the wave front in which the amplitude takes considerably larger values than elsewhere, but it does not appear probable that this has any direct bearing on the mechanism of the photoelectric effect, as appears possible at first sight.

I wish to thank Dr. Bromwich for his criticism and advice in connexion with this paper.

L. *The Motion of Electrons in Gases under Crossed Electric and Magnetic Fields.* By RABINDRA N. CHAUDHURI, M.Sc., Ph.D., King's College, London\*.

IT has been shown in a previous paper by Richardson and Chaudhuri† that a certain magnetic field acting perpendicular to the electric intensity large enough to stop the electron current (in vacuum) between a hot wire and a concentric anode, is insufficient when there is a trace of gas present. This effect occurs even below the ionization potential of the surrounding gas. It was shown, at least in air and in nitrogen, that the residual current could be accounted for as largely due to the collisions between electrons and gas molecules. It might, however, be also due to the formation of heavy ions by the slow-velocity electrons combining with gas molecules, and the magnetic field being insufficient for the heavy ions, the latter find their way to the anode. So that in any case the magnitude of the residual current should be some characteristic of the gas. In the following, two important gases, A and CO, have been studied.

As before, the source of electrons was a tungsten filament (radius  $a$ ) stretched along the axis of a cylindrical anode (radius  $b$ ). The electric field (potential difference  $V$ ) was applied between the hot wire and the anode, and the magnetic field  $H$  was parallel to the filament, so that the electric and magnetic fields were perpendicular to each other. Under these conditions, the electrons will describe a cycloidal spiral about the filament, and the maximum distance attained by the electron will be given by

$$H^2 = \frac{8V \cdot \log r/a}{e/m \cdot r^2 \cdot \log b/a} + \frac{8V_1}{e/m \cdot r^2}, \quad \dots \quad (1)$$

where  $V_1$  = the voltage equivalent to the initial velocity of the electrons.

Substituting the values of  $e/m$ , and  $a$  ( $=0.005$  cm.), and  $b$  ( $=1.0$  cm.), we get

$$H^2 = \frac{8.4V \cdot \log r/a}{r^2} + 45.0 \frac{V_1}{r^2}, \quad \dots \quad (2)$$

where  $V$  and  $V_1$  are in volts.

\* Communicated by Prof. O. W. Richardson, F.R.S.

† Phil. Mag. Feb. 1923, p. 337.

‡ This number was erroneously given in the last paper as 89.



The accelerating potential applied between the filament and the anode in these experiments was 4.2 volts, and taking the maximum initial velocity possessed by a measurable number of electrons as 1.5 volts, we get

$$H^2 = \frac{35.28 \log r/0.005}{r^2} + \frac{67.5}{r^2} \dots (3)$$

Thus we see, if there is no gas present, when a magnetic field of 160 units is used, then the maximum velocity electrons will be confined within a distance of 0.096 cm., and zero velocity ones will be within 0.06 cm., from the axis of the hot wire.

But if, however, any traces of gas are present, the electrons might combine with gas molecules and will find their way to the anode as heavy ions, the magnetic field necessary to stop the electrons being now insufficient (more than 4000 would be required); or, it might be that the electrons on their way have their velocity altered by a collision so as to cause them to move in new spiral paths about an axis parallel to the magnetic field. In this way by a repeated number of collisions, they might ultimately reach the anode. If, however, the latter supposition is true, we should be able to find out the length of the mean free path of the electrons in this particular gas.

#### *Description of the Apparatus.*

The thermionic tubes used in these experiments are the same as before, and the filament and cylindrical anode are of the same material and dimensions. The tube was connected with the gas-generating part by means of glass tubing, so that it might not be contaminated while being transferred (see previous paper, page 342). The inlet *i* of the apparatus was connected through a liquid-air trap *L* to a quartz tube containing two porcelain boats in which some small bits of calcium are kept to prepare Argon from air. There is a glass tube containing a copper spiral which can be heated electrically to absorb oxygen. This in turn is joined to a set of apparatus to obtain carbon monoxide, etc. It is essential in these experiments to have the gas as pure as possible, and that is why the thermionic tube was connected with the gas-generating part by means of glass tubing. Care was taken as much as possible to avoid any greased taps. The electrical connexions and the rest of other details were the same as before.

*Experiments in Argon.*

Argon was obtained by two different ways: one sample was supplied by the British Oxygen Company, and the other was prepared from air in the Laboratory. The first sample was let in through the inlet *i*, and was allowed to wash the whole apparatus for several minutes. Afterwards closing the inlet, the gas was pumped out to a fraction of a mm. pressure; the filament was then heated and the anode bombarded in the usual way. The calcium tube was next heated gradually, by which impurities in argon like O, N, CO<sub>2</sub>, etc., are absorbed. The calcium tube should not be heated continuously, as it is found that hydrogen diffuses through it when it is very hot. The difficulty of preparing argon free from traces of hydrogen or nitrogen is very great—when the argon lines only are seen in the spectrum tube, the gas is experimented upon, otherwise the process is repeated till pure gas is obtained. Argon was also prepared from air in the laboratory, by introducing air through *i* and then pumping down to a few mm. pressure. The calcium tube is then heated to absorb other constituents of air. In both cases, the same sort of result was obtained when the gas used was very pure.

The following results were obtained, when only the argon lines were visible. Liquid air was kept in the traps LL.

TABLE I.

Accelerating Potential = 4.25 volts.

Heating Current on the filament = 1.25 amp.

Pressure inside the tube.	Saturation Current without magnetic field.	Residual Current with magnetic field.	Magnetic Field.	Percentage of Residual to Saturation Current.
$230 \times 10^{-4}$ mm.	$4200 \times 3 \times 10^{-10}$ amp.	$8.5 \times 3 \times 10^{-10}$ amp.	160	0.20
150 "	4200 "	6.5 "	"	0.15
85 "	4680 "	5.0 "	"	0.11
48 "	4440 "	0.5 "	"	0.01
28 "	4560 "	0.0 "	"	0.00

These results are plotted in fig. 1 (A), and it will be seen that the percentage is very little indeed. But the

results like the above are very difficult to get; usually, however, the following sort of values of the percentage are found.

Fig. 1.

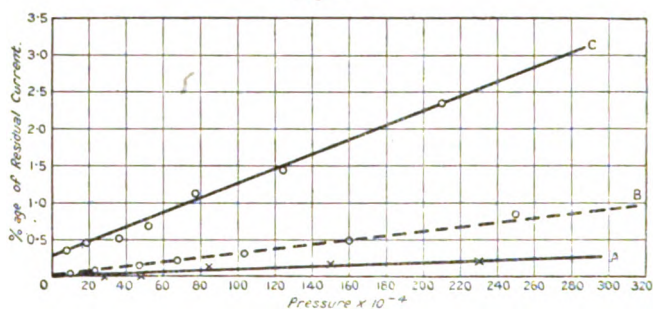


TABLE II.

Accelerating Potential = 4.2 volts.

Heating Current = 1.20 amp.

Pressure inside the tube.	Saturation Current without magnetic field.	Residual Current with magnetic field.	Magnetic Field.	Per-centage.
$389 \times 10^{-4}$ mm.	$1932 \times 3 \times 10^{-10}$ amp.	$28.0 \times 3 \times 10^{-10}$ amp.	160	1.4
250 "	1890 "	15.5 "	162	0.82
160 "	1896 "	9.0 "	160	0.47
103 "	1899 "	6.3 "	160	0.31
67 "	1920 "	4.0 "	164	0.20
47 "	1920 "	3.0 "	164	0.15
23 "	1920 "	1.6 "	164	0.08
10 "	1920 "	0.7 "	164	0.04

These values are plotted in fig. 1 as the dotted line (B), which gives a higher percentage than before. However, both these are exceptionally small in comparison with air or nitrogen (*e. g.* for air 15.0, and nitrogen 12.9, at  $100 \times 10^{-4}$  mm.).

It is also interesting to see what happens if there is some vapour present, such as that of water, grease, or mercury, as is sometimes found if the liquid air is not kept in the traps. The following results were obtained when liquid air was NOT kept in the traps, and the argon was not very pure.

TABLE III.

Accelerating Potential = 4.25 volts.

Heating Current = 1.3 amp.

Pressure inside the tube.	Saturation Current without magnetic field.	Residual Current with magnetic field.	Magnetic Field.	Percentage.
$330 \times 10^{-4}$ mm.	$1500 \times 3 \times 10^{-10}$ amp.	$70.0 \times 3 \times 10^{-10}$ amp.	164	4.66
210 "	1530 "	36.0 "	166	2.35
124 "	1530 "	22.0 "	166	1.44
77 "	1660 "	17.0 "	164	1.09
51 "	1620 "	11.5 "	164	0.71
35 "	1680 "	8.5 "	166	0.52
18 "	1680 "	7.5 "	164	0.44
8 "	1680 "	6.0 "	164	0.35

These points are plotted in fig. 1 on the top (C). It will be seen here that there is a perceptible amount of residual current even when the recorded pressure is zero.

Thus we see when the argon used is very pure and not contaminated with any vapour, the amount of residual current in a crossed electric and magnetic field is very little indeed in comparison with other gases. We shall, however, discuss this later on.

#### *Experiments in Carbon Monoxide.*

In order to study the effect in some other gas, carbon monoxide was chosen, because of its similarity with some of the properties of nitrogen. The gas was prepared in the same apparatus as that used for nitrogen (previous paper). Fresh  $P_2O_5$  and KOH bulbs were joined, and the portions of the glass apparatus to prepare the gas were washed very carefully with distilled water so that traces of the other gases might not be left there. The carbon monoxide was obtained by the action of pure sulphuric acid on formic acid. Care was taken in collecting the gas that no air-bubbles remained on the top of the liquids, and several portions of the gas collected were pumped out. Afterwards, some gas was kept over the drying  $P_2O_5$  and KOH bulbs for a few days before passing into the experimental tube. By this, water, sulphuric, sulphurous, or carbonic acid vapour will be absorbed by the KOH bulb, and the pentoxide will also help to keep the gas dry. Now, a little of the gas is introduced and pumped down to  $300 \times 10^{-4}$  mm. pressure, and the copper spiral is heated to absorb any oxygen that might contaminate the CO. After heating the filament the wire and the tube are ready for the experiment. The following

*Phil. Mag.* S. 6. Vol. 46. No. 273. Sept. 1923. 2 H

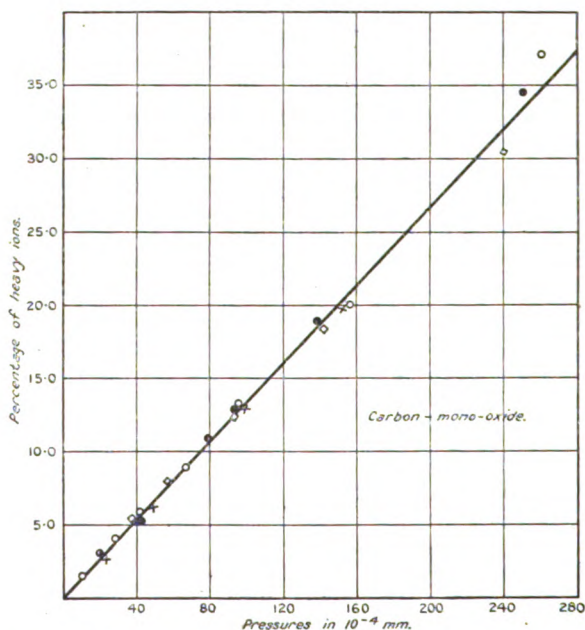


results were obtained with carbon monoxide when liquid air was kept in the traps and they were found to repeat invariably.

TABLE IV.  
Accelerating Potential = 4.1 volts.  
Filament Current = 0.95 amp.

Pressure inside the apparatus.	Saturation Current without magnetic field.	Residual Current with magnetic field.	Magnetic Field.	Per-centage.
$260 \times 10^{-4}$ mm.	$470.4 \times 3 \times 10^{-10}$ amp.	$175 \times 3 \times 10^{-10}$ amp.	164	37.2
156 "	537.6 "	107 "	165	20.0
98 "	556.8 "	74 "	164	8.9
67 "	528.0 "	47 "	162	5.9
42 "	508.0 "	30 "	162	5.9
28 "	518.4 "	21.5 "	160	4.1
10 "	528.0 "	8 "	160	1.5

Fig. 2.



These results are plotted in fig. 2. It will be seen here that the percentage of the residual current is very nearly the same as that in nitrogen (see Phil. Mag. Feb. 1923, p. 349). It might be supposed that the CO is contaminated by nitrogen, but as there was hardly any diminution of pressure when the copper spiral was heated, it shows the absence of air and so of nitrogen. Hence there is no doubt about the

purity of the carbon monoxide. The points marked as ○ are for the data given above, and the other points are given by subsequent experiments.

For comparative purposes it might be of some interest to tabulate the values of the residual currents with different gases, when the conditions are more or less the same.

TABLE V.

Gas.	Percentage at $2.0 \times 10^{-4}$ mm.	Percentage at $60 \times 10^{-4}$ .	Percentage at $100 \times 10^{-4}$ .	Percentage at $200 \times 10^{-4}$ .
Air .....	0.4	9.0	15.0	29.8
Nitrogen .....	0.3	7.9	13.0	26.0
Carbon monoxide. .	0.3	8.0	13.3	26.8
Argon .....	0.00	0.0	0.1	0.2

### *Residual Current and the Velocity of the Impinging Electron.*

It must have been noticed that we have always used the same accelerating potential for the electrons, as well as the same magnetic field to curl them up. This was done to compare the percentage (of residual current to the initial saturation current) in different gases, when the velocity of the impinging electron and its length of path in the gas (so that it meets with the same number of molecules) are the same. The next point of importance would be to see how far the percentage depends on the velocity of the electron. This was studied in carbon monoxide and the results are given below.

In our thermionic tube we had the magnetic field parallel to the hot wire, so that the electrons were curling round it. But, as the electrons are emitted with all velocities, the zero-velocity ones will be nearest and the highest-velocity ones producing a detectable current farthest away from the hot wire, under the action of the fields. We can adjust the values of  $H$  and  $V$  in such a way that, when the velocity of the impinging electron is increased, the maximum distance  $r$  from the wire, along its axis, is kept the same.

Thus we had, from (1)

$$H^2 = \frac{8V \log r/a}{e/m \cdot r^2 \log b/a} + \frac{8V_i}{e/m \cdot r^2}.$$

Taking  $H = 160$ ,  $V = 4.2$  volts, and average initial energy corresponding to 1.5 volts, we had  $r = .095$  cm. Now, if we keep  $r$  the same, we can find out what value of  $H$  will correspond to any other potential. It is found that

$$H^2 = 2735.9V + 14770,$$

where  $V$  is in volts.

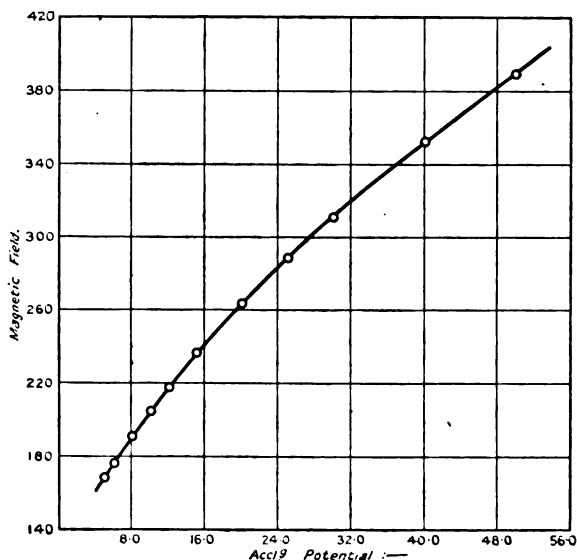
In the following table are given the values of  $H$  corresponding to different accelerating potentials, so that the electrons are always kept at the same distance,  $\cdot 095$  cm., from the hot wire, and consequently the length of the path of the electrons in the gas is the same.

TABLE VI.

Accelerating Potential.	Magnetic Field.
5 .....	168.7
6 .....	176.6
8 .....	191.5
10 .....	205.2
12 .....	218.2
15 .....	236.3
20 .....	263.6
25 .....	288.4
30 .....	311.2
40 .....	352.7
50 .....	389.3

These values are plotted in fig. 3, which can be used as a sort of calibration curve.

Fig. 3.



The following are the results of experiments in carbon monoxide. The gas was prepared in the usual way, and all precautions were taken to keep the pressure constant while the gas was examined. Liquid air was kept in the traps to stop the advance of any vapour into the thermionic tube.

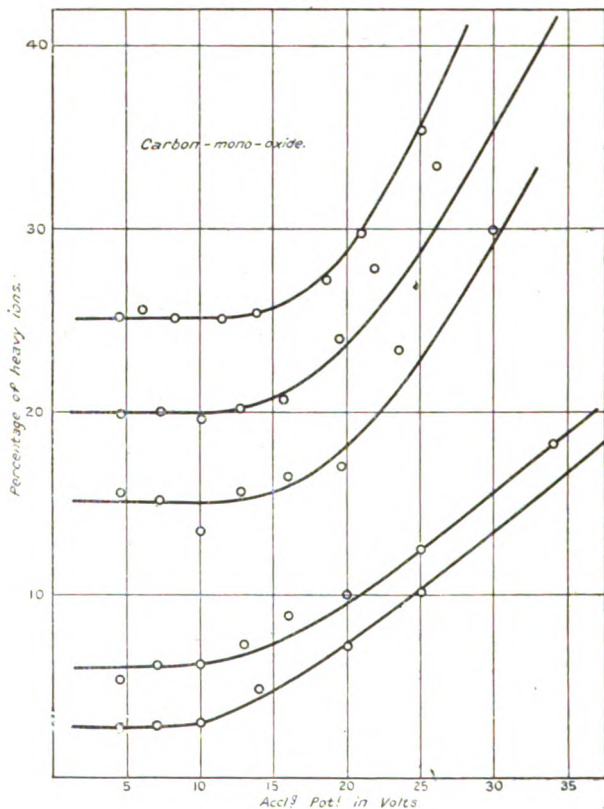
TABLE VII.  
Heating current=0.95.

Accelerating Potential.	Saturation Current without magnetic field.	Residual Current with magnetic field.	Magnetic Field.	Percentage.
Pressure = $168 \times 10^{-4}$ mm.				
4.5 volts	444 $\times 3 \times 10^{-10}$ amp.	112 $\times 3 \times 10^{-10}$ amp.	166	25.2
7.0 "	444 "	114 "	184	25.6
8.3 "	432.9 "	108 "	194	25.0
9.0 "	455.1 "	114 "	198	25.1
11.5 "	457.3 "	115 "	214	25.1
13.8 "	456.6 "	116 "	228	25.4
18.5 "	460.3 "	126 "	255	27.3
21.0 "	466.2 "	139 "	272	29.8
25.0 "	481.0 "	170 "	295	35.3
Pressure = $124 \times 10^{-4}$ mm.				
4.5 volts	427 $\times 3 \times 10^{-10}$ amp.	85 $\times 3 \times 10^{-10}$ amp.	166	19.9
7.0 "	458 "	92 "	184	20.0
10.0 "	406 "	79 "	205	19.4
12.8 "	406 "	83 "	224	20.4
15.5 "	420 "	87 "	240	20.7
19.5 "	420 "	101 "	264	24.0
21.7 "	406 "	113 "	276	27.8
29.0 "	409.5 "	138 "	310	33.7
Pressure = $82 \times 10^{-4}$ mm.				
4.5 volts	510.3 $\times 3 \times 10^{-10}$ amp.	60 $\times 3 \times 10^{-10}$ amp.	166	13.4
7.2 "	542.7 "	72 "	186	15.1
10.0 "	530.6 "	62 "	205	13.3
12.7 "	534.6 "	73 "	225	15.5
16.0 "	502.2 "	73 "	242	16.5
19.7 "	534.6 "	80 "	265	17.0
23.5 "	550.8 "	113 "	284	23.4
30.0 "	567.0 "	147 "	315	29.9
Pressure = $34 \times 10^{-4}$ mm.				
4.5 volts	481.3 $\times 3 \times 10^{-10}$ amp.	28 $\times 3 \times 10^{-10}$ amp.	166	5.3
7.0 "	508.2 "	31 "	184	6.1
10.0 "	496.7 "	31 "	205	6.2
13.0 "	215.9 "	38 "	225	7.3
15.9 "	492.9 "	44 "	242	8.9
20.0 "	512.1 "	51 "	266	9.9
25.0 "	519.8 "	65 "	290	12.5
34.0 "	575.9 "	94 "	335	18.2
Pressure = $14 \times 10^{-4}$ mm.				
4.5 volts	406 $\times 3 \times 10^{-10}$ amp.	11 $\times 3 \times 10^{-10}$ amp.	166	2.7
7.0 "	413 "	12 "	184	2.9
10.0 "	399 "	12 "	205	3.0
14.0 "	413 "	20 "	230	4.8
20.0 "	402.5 "	29 "	265	7.2
25.0 "	434 "	44 "	290	10.1
34.0 "	476 "	87 "	336	18.3



All these results are plotted in fig. 4. It will be seen from these curves that the percentage tends to keep fairly constant up to a certain voltage, about 10 in our case, after which the residual current begins to increase. The ionization potential of CO is also 10 volts. What happens, I believe, is, when the velocity reaches the ionization potential,

Fig. 4.



some more electrons are produced which in turn might form some fresh heavy ions, or these electrons, being knocked off near the electrode, find their way to the anode.

Thus we see that the percentage of residual current does not depend on the velocity of the impinging electron up to a certain limit, viz., the ionization potential, after which the result becomes complicated by other phenomena.

## Discussion.

The most interesting results of these investigations are the comparatively small magnitude of the residual current in argon under the same conditions as in other gases, and approximately the same amount in carbon monoxide as in nitrogen. It was suggested in the previous paper (*loc. cit.*) that the formation of heavy ions is relatively unimportant in comparison with the collision of electrons with gas molecules. Under the conditions of the experiment, it is found that when a collision has once taken place, the electrons cannot go back to the hot wire, nor can they accumulate in the field, and the only place to go to would be the anode after a repeated number of collisions. However, if this view is correct, we should be able to get an approximate idea of the mean free path of an electron in the gas concerned.

To do this, we require to know the length of the path ( $s$ ) of an electron in the magnetic field when no collision occurs. We can take, approximately, this to be equal to an arc of a circle whose radius is equal to the maximum distance  $r$  which the electron travels from the axis. Then

$$s = r(\pi - 2 \sin^{-2} a/r),$$

where  $a$  is the radius of the hot wire.

If we suppose the length of the mean free path of an electron is the same under the action of the fields as that when they are absent, then the proportion  $\xi$  which collide in path  $s$  is

$$\xi = \int_0^s e^{-\frac{x}{\lambda}} \frac{dx}{\lambda} = 1 - e^{-\frac{s}{\lambda}}.$$

$$\therefore \lambda = -s/\log_e(1-\xi).$$

When  $H=160$ ,  $r=0.08$  as the mean of the distances of the electrons from the wire, we get

$$s = 0.08 \times 3.015 = .24120 \text{ cm.}$$

Now at  $100.10^{-4}$  mm. pressure,  $\xi$  for argon is 0.01, and for CO is 0.867. Then we get

$$\lambda_{\text{argon}} = 24.12 \text{ cm.}$$

$$\text{and } \lambda_{\text{CO}} = 1.69 \text{ ,,}$$

$$\text{i. e., } \lambda_{\text{argon}} \text{ at } 760 \text{ mm.} = 32.0 \times 10^{-5} \text{ cm.,}$$

$$\lambda_{\text{CO}} \text{ ,, ,, } = 2.2 \times 10^{-5} \text{ ,,}$$

From the Kinetic Theory, taking the diameters of molecules, we get  $\lambda_{\text{argon}} = 3.6 \cdot 10^{-5}$  and  $\lambda_{\text{CO}} = 3.25 \cdot 10^{-5}$ , and it will be seen that the mean free path of an electron in argon is about 10 times that deduced from the Kinetic Theory

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from molecular data. Also, the mean free path in carbon monoxide is of the same order of magnitude as that obtained from Kinetic Theory.

In some experiments on the motion of electrons in hydrogen (shortly to be communicated) it was found that the mean free path in molecular hydrogen is about  $1.24 \times 10^{-5}$  cm. Thus the mean free path in argon is more than 20 times that in hydrogen. An abnormally large value of the free path in argon has also been observed by Townsend and Bailey \*. They found, after making corrections for the velocity of agitation of electrons in the electric field, that the mean free path in argon is about 60 times larger than that in hydrogen.

However, this apparent disagreement of the mean free path of an electron in argon from that given by the Kinetic Theory cannot be explained, even if we take into consideration the temperature of the gas in which the electrons are moving.

### *Summary.*

In this paper we have seen that when electrons are moving through any gas, the current between the emitting source and the anode is not stopped by a magnetic field (large enough to stop the current in vacuum) acting perpendicular to the electric intensity.

In argon the residual current is very small, whereas in carbon monoxide the fraction is fairly large: *e. g.*, at  $100.10^{-4}$  mm. pressure the percentage in argon is 0.1, whereas in carbon monoxide it is 13.3.

It has been also found, when the velocity of the impinging electron is increased, that the percentage of the residual current does not increase, at least up to the ionization potential of the gas (CO). After that potential, the percentage of residual current increases.

Assuming the residual current is due to the electrons colliding several times with gas molecules, it is possible to find an expression for the mean free path of the electron; and the value found in CO agrees fairly with that deduced from Kinetic Theory.

An abnormally large free path is obtained in argon, and the value obtained is about 10 times more than that obtained from the Kinetic Theory.

In conclusion, I wish to express my gratitude to Prof. Richardson for his suggestions and advice during the course of this work.

\* Phil. Mag. vol. xliii. p. 1127.

II. *Low-velocity X-ray Electrons.* By LEWIS SIMONS, D.Sc. Reader in Physics in the University of London\*.

1. **W**HILST studying the absorption of X-ray electrons in various gases certain peculiarities in the absorption curves led me to conclude that groups of electrons, as predicted by O. W. Richardson †, possessing speeds less than that given by the equation

$$\frac{1}{2}mv^2 = h\nu, \quad . \quad . \quad . \quad . \quad . \quad . \quad (i)$$

where  $\nu$  is the maximum frequency of the incident radiation, played an important rôle in electronic emission†. Further work on this subject by the writer§ and by de Broglie|| and Whiddington¶ showed conclusively that the maximum speed of each sub-group could be represented by the equation

$$\frac{1}{2}mv^2 = h(v - \nu_0), \quad \dots \dots \dots \text{(ii)}$$

where  $\nu_0$  represents the frequency of the radiation associated with the level within the atom from which the electron is ejected, the value of which is determined from a knowledge of the X-ray spectrum of the element emitting the electrons. The validity of this equation has been confirmed in the region of  $\gamma$ -ray frequencies by Ellis \*\*. It marks the position of the head of each  $\beta$ -ray spectral line. It would be very difficult to determine the width of these lines or bands, whilst equation (ii) indicates that there should be no lower limit to the velocity of photo-electrons.

2. The experiments described were directed to the determination of the distribution with velocity of those electrons emerging with minimum energy from a screen of high atomic weight when irradiated with X-rays. They have shown that, in point of number, of the electrons described in paragraph 1 practically all the emission is confined to those of velocity less than 2 volts. I have therefore employed a retarding electrostatic field method, such as is described by Richardson and Brown†† in their study of the distribution of the normal

\* Communicated by the Author.

† Proc. Roy. Soc. A. xciv. p. 272 (1918).

† Trans. Roy. Soc. S. Africa, viii. (1) p. 73 (1919).

§ Phil. Mag. xli. p. 121 (1921).

|| *Comptes Rendus*, clxxii. pp. 274, 527, 764, 806 (1921); *Journal de Physique*, vi. T. ii. p. 265 (1921).

† *Phil. Mag.* xliii. p. 1116 (1922).

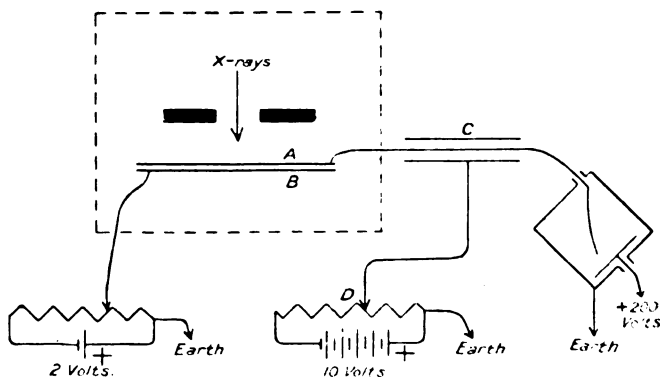
\*\* Proc. Roy. Soc. A. xcix. p. 261 (1921), ci. p. 1 (1922).

†† *Phil. Mag.* xvi. p. 353 (1908).

component of the velocity of thermions emitted from a comparatively small surface of hot platinum towards an extensive plane opposite. In the corresponding X-ray experiment the electronic currents measured were necessarily much smaller, and, moreover, no variation of the opposing electrostatic field, caused, for example, by the charging of an electrometer, could be allowed during a run. A "null" method of employing a tilted electroscope was therefore devised and other precautions employed that are given below.

3. In fig. 1, A and B represent two sheets of filter-paper, each about 16 sq. cm. in area, insulated from each other and about 1 mm. apart. The side of A remote from B was made conducting by rubbing with pure graphite. The side towards B was coated with one sheet of ordinary gold-leaf.

Fig. 1.

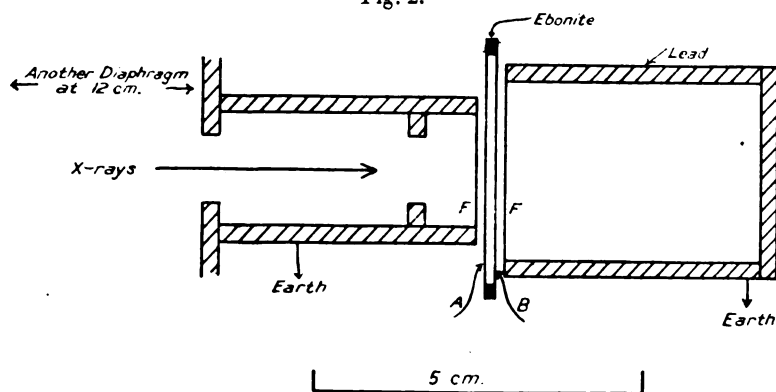


Both faces of B were rubbed with graphite; whilst this makes the surface a good conductor, I have never been able to detect any electronic emission from it. The gold-leaf of the screen A was connected directly to a Wilson's tilted electroscope by a short lead sheathed for 10 cm. of its length with an insulated metal tube 2 cm. in diameter, the potential of which could be varied continuously from 0 to  $-10$  volts by turning a handle on the continuous rheostat D. The potential of B could be maintained steady at any desired value. It was not varied beyond the range  $\pm 2$  volts.

4. The method of experimenting was as follows:—After the gold-leaf system with A attached had been earthed and insulated, C earthed, and B at, say,  $-1$  volt, the X-ray beam was started. The system A would normally begin to

acquire a positive potential due to loss of electrons from the gold. This change of potential was prevented by continuously diminishing the potential of C from zero downwards, so that the potential of the insulated gold-leaf system remained at zero during the run, as denoted by the stationary position of the needle of the electroscope on the eyepiece scale. After the one-minute run was over C was earthed, A at once acquired its normal positive potential due to loss of negative charge, the deflexion of the electroscope needle giving a measure of this charge after suitable calibration. Thus the arrangement might be called a "null" method of using an electroscope. It was extremely useful, for it quite got over the difficulty involved in measuring the rate of charging of A without the potentials of A or B

Fig. 2.



Arrangement of Lead Stops and Radiator A, within evacuated chamber.

varying. Its advantages are obvious in the accurate measurement of extremely low electronic speeds. Incidentally, it might also be noted that the final position of the jockey on D maintaining A at zero potential at the end of the run is also a measure of the charge acquired by A.

5. Great precaution was taken to avoid the spurious charging of A by electronic emission from any part of the apparatus other than the gold-leaf upon it. The X-ray beam was rendered parallel by means of three lead stops and limited to a cross-section area of 1 sq. cm. The last lead stops, the sheets A and B, and the general arrangements are shown in fig. 2, the whole system being enclosed in an exhausted brass cylinder lined inside with filter-paper.

All lead parts were given a thin film of paraffin-wax and earthed. F, F are sheets of graphited filter-paper, about 1 mm. from A and B respectively, placed there for the double purpose of limiting the volume in the neighbourhood of A and of screening it from stray electrostatic fields. That the whole arrangement was quite successful for the purpose for which it was intended was determined by replacing A by an exactly similar sheet, but without the gold-leaf upon it. On now making a run in a manner described above, even under the most favourable conditions with B charged positively, no readable deflexion could be obtained. The readings could therefore be plotted without any corrections or adjustments. To approach ideal conditions, the area radiating electrons must be small in comparison with the whole area of the parallel plates used for testing their speeds. The effect of increasing the area of these plates is to diminish the currents measured. To obtain measurable currents the full radiation from a tungsten target "radiator" pattern (Coolidge tube was employed, the tube being excited by means of a transformer.

6. Two characteristic curves are shown in fig. 3, the ordinates representing the charge acquired in 1 minute by the system A, maintained at zero potential, the abscissæ give the potential of B in volts. Curve I is for a current of 2 milliamperes through the tube, curve II for 3.5 milliamperes. The points on the two curves were taken alternately and after equal intervals of time, the heating current of the cathode of the Coolidge tube being maintained during the whole experiment and varied slightly for alternate points to give the above outputs. The smoothness of the two curves indicates the accuracy of the observational points.

7. Both curves show that 85 per cent. of the electrons emitted have velocities less than that given by a fall through 2 volts, and the argument against their being true dependent photo-electrons described in paragraph 1 is as follows:—The results are complicated by the incident radiation being heterogeneous, but M. and L. de Broglie have shown from considerations of the absorption law of Bragg and Peirce\* that selective absorption of frequency  $\nu$  will occur when  $\nu = \frac{1}{3}\nu_0$ , where  $\nu_0$  is a natural frequency existing in an absorbing element. Taking this to be the  $I_{a1}$  frequency for gold (w.l. =  $1.27 \times 10^{-8}$  cm.), the major velocity of the dependent electrons emitted in these experiments should be

\* *Comptes Rendus*, Sept. 1921, p. 527.

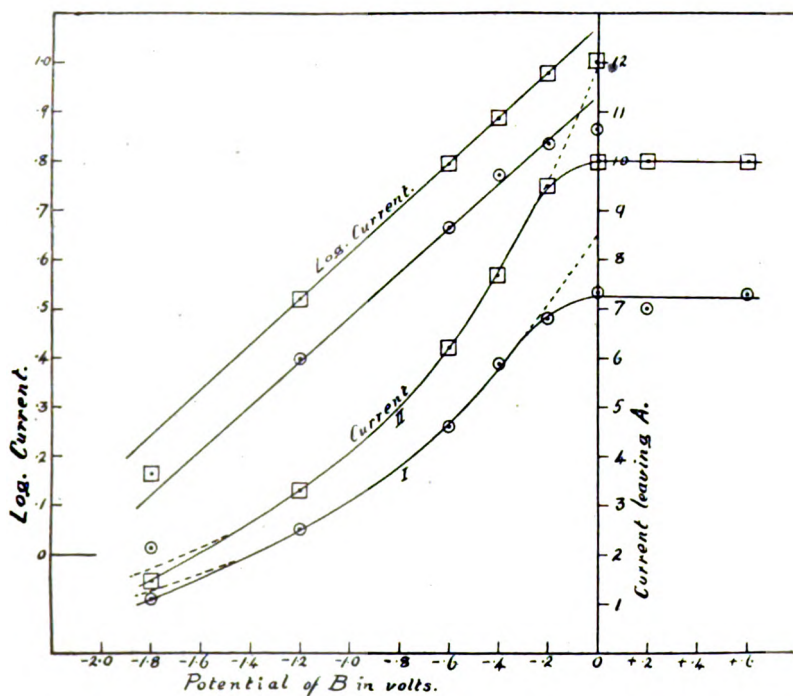
given by

$$Ve = h(\nu - \nu_0) = h\nu_0/3 \quad \dots \quad (iii)$$

$$\therefore V = 3.35 \times 10^3 \text{ volts.}$$

The curves show that this cannot be the case. Considering now that the energy-distribution curve for the radiation from the Coolidge tube is continuous, it follows that residues such as (iii) will also form a continuous series, but, as the

Fig. 3.



major number of electrons emitted have comparatively zero speed, if these were the true photo-electrons, then the emission spectrum from the Coolidge tube should correspond exactly to that from gold. Again, interesting results on these low-speed electrons have recently been obtained by Shearer\*, though the design and method of using of his

\* Phil. Mag. xlv. p. 806 (1922).



apparatus differ from that described herein in many important respects, the present design, described above, being especially adapted to the measurement of the normal component of the velocities of the slowest rays. His general conclusions are that these electrons may be called independent, that their properties are similar to those of the  $\delta$ -rays produced by  $\alpha$ -rays, and that they are produced by the intermediary rapid  $\beta$ -rays. Two other factors that might enter must be considered. The first is the effect of the secondary X-rays from the gold. In a previous paper \* the writer has shown that this must be too small to produce a major effect, and the most frequent normal component of the speed, being in the neighbourhood of 0.48 volt, corresponds to ionization by rays in the visible region of the spectrum if we use the value  $3 \times 0.48$  volts to calculate the mean resultant energy of these slow rays. The second effect is due to the thermal reaction accompanying the recoil of an atom emitting a rapid  $\beta$ -ray. Interest in this subject has been renewed recently by P. L. Kapitza †, who has shown that the slow electronic  $\delta$ -radiation arising from the impact of  $\alpha$ -particles is due to thermal effects arising from localized points of impact, the intermediary being high-speed electrons. Richardson's thermionic equations are applied to the resultant distribution of  $\delta$ -radiation, and temperatures of the order  $20,000^\circ$  abs. are assigned to the centres yielding the observed most probable speed.

8. If the distribution of speeds is Maxwellian, the current received by the plate opposite the radiator, and therefore that leaving the radiator designed as described in paragraph 3, is governed by the equation ‡

$$\log_e i/i_0 = - \frac{ne}{RT} V_1, \quad \dots \dots \dots (iv)$$

where  $n$  is the number of molecules in 1 c.c. of a perfect gas at  $0^\circ$  C. and 760 mm. pressure,  $R$  is the gas constant for this quantity of gas,  $V_1$  is the retarding potential reducing the current from  $i_0$  to  $i$ ,  $ne = 43$  e.m. unit,  $R = 3.7 \times 10^3$  erg/deg. C. The curves show how far the distribution in speeds differs from the logarithmic distribution represented by the dotted lines in fig. 3. It should be pointed out here

\* Phil. Mag. xli. p. 130 (1921).

† Phil. Mag. xlv. p. 989 (1923).

‡ O. W. Richardson, 'The Emission of Electricity from Hot Bodies,' 1916, p. 144.

that no special preparation of the surface to ensure cleanliness was possible, and the vacuum maintained was of the order  $\cdot 01$  cm. of mercury. These two factors would probably account for the loss of a fraction of the very slowest electrons, indicated by a bending over of the curves to the current axis. Assuming that the curves are logarithmic over the major part of their length and that the process of emission can be compared with the thermionic process, we have from both curves using formula (iv)  $T = 1.1 \times 10^4$  deg. abs.

9. That atomic recoil can scarcely account for this high temperature is shown as follows:—The velocity of recoil of a stationary atom of mass  $M$  yielding an electron of energy  $eV$  will be  $(2meV)^{1/2}/M$ . In the present case  $M = 197 \times 1.66 \times 10^{-24}$  gm. for a gold atom,  $V = 4.4 \times 10^4$  volts, being the peak potential supplied to the Coolidge tube, and hence the velocity of recoil  $= 3.4 \times 10^4$  cm./sec. as compared with an average velocity of  $1.89 \times 10^4$  cm./sec. due to the thermal motion of gold atoms at  $15^\circ$  C. A simple calculation shows that under the most favourable circumstances of recoil, *i. e.*, when the direction of motion of the ejected electron is opposite to that of thermal motion of the atom, and therefore the above velocities will be added, the resulting energy of the atom cannot be greater than that corresponding to  $2300^\circ$  abs. The approximate average velocity corresponding to a temperature of  $1.1 \times 10^4$  deg. abs. is  $11.6 \times 10^4$  cm./sec., and consequently an atom would need a thermal velocity of  $(11.6 - 3.4) \times 10^4$  cm./sec. at least before recoil in order to acquire this temperature. Taking this velocity, *viz.*  $8.2 \times 10^4$  cm./sec. and the average velocity at normal temperature as  $1.89 \times 10^4$  cm./sec., the ratio is 4.3. The ratio of the number of atoms whose velocities lie between  $4.3u$  and  $4.3u + du$  to those that lie between  $u$  and  $u + du$ , where  $u$  is the root mean square of the velocity of the atoms, from Maxwell's distribution law is then only of the order  $10^{-10}$  to 1. This, together with the fact that very few of all the atoms present are influenced by the radiation, rules out the possibility of centres acquiring the extremely high temperature of  $1.1 \times 10^4$  deg. abs. by recoil alone.

10. We are therefore left to account for the experimental observations in some such manner as follows. The original form of the energy is that of the fast-moving  $\beta$ -rays, the final form is energy of the same type but degraded. The primary  $\beta$ -ray of large energy yields a large number of slow  $\beta$ -rays all of similar origin—or  $\delta$ -rays, as they have been

called,—energy corresponding to that of the ionization potential being taken from the parent store at each inelastic impact. Only the most loosely bound electrons are affected. The mechanism of the interchange of energy is difficult to conceive, but colour is lent to this view by the fact that C. T. R. Wilson's tracks of  $\beta$ -particles are unforked, *i.e.* a rapid  $\beta$ -ray only produces by impact with atoms other  $\beta$ -rays or ions whose energy is very small in comparison with that of the parent particle. Very rarely does a large change of energy by direct impact occur. The logarithmic distribution of the particles will be the subject of further investigation.

#### *Abstract.*

It is shown that the normal component of the velocity of over 85 per cent. of the electrons emitted from a gold film under the influence of a heterogeneous beam of X-rays is less than 2 volts. The distribution with velocity bears a relationship to that of the thermions from a hot body. It is argued that the mode of production of these slow electrons can scarcely be due to atomic recoil consequent on the ejection of a rapid  $\beta$ -ray nor to the action of the transformed X-ray energy into energy of longer wave-length. The analogy with the thermionic process probably arises from the fact that in both cases only the outermost system of electrons take part in the action, though the mechanism of the two processes must differ considerably, in the present case the intermediary being the rapid primary  $\beta$ -ray.

The distribution with velocity of the electron atmosphere, from the point of view of thermionics in the case investigated, corresponds to a temperature of  $11,000^{\circ}$  abs. It becomes important, therefore, to investigate under all conditions the correspondence between the two processes.

A "null" method of using an electroscope is described.

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LII. *Two Solutions of the Stress Equations, under Traction only, expressed in general Orthogonal Coordinates, with two deductions therefrom.* By R. F. GWYTHYER, M.A.\*

THIS paper is in continuation with a portion of one entitled "An Analytical Discrimination of Elastic Stresses in an Isotropic Body" †, and I employ the same notation {P, Q, R, S, T, U} for stress and {e, f, g, a, b, c} for strain. There are two solutions, one giving the elements of stress in terms of three functions  $\theta$ , and one in terms of three functions  $\psi$ , each of them being general solutions. As there will be no transformation of coordinate axes, the two solutions will be considered separately. I now find that I should have attributed the  $\theta$ -solution in Cartesians to Maxwell, and the  $\psi$ -solution to Morera.

Ultimately I combine the two solutions to derive the six equations of identity connecting the differential coefficients of the elements of strain in an orthogonal coordinate system.

1. I propose to find the solution, step by step, of the stress-equations, under tractions only, which I shall consider in the form

$$\begin{aligned} \frac{\partial}{\partial \xi} \left( \frac{P}{h_2 h_3} \right) + h_1 \frac{\partial}{\partial \eta} \left( \frac{U}{h_3 h_1^2} \right) + h_1 \frac{\partial}{\partial \zeta} \left( \frac{T}{h_1^2 h_2} \right) \\ + \frac{1}{h_2^2 h_3} \frac{\partial h_2}{\partial \xi} Q + \frac{1}{h_2 h_3^2} \frac{\partial h_3}{\partial \xi} R = 0, \\ h_2 \frac{\partial}{\partial \xi} \left( \frac{U}{h_2^2 h_3} \right) + \frac{\partial}{\partial \eta} \left( \frac{Q}{h_3 h_1} \right) + h_2 \frac{\partial}{\partial \zeta} \left( \frac{S}{h_1 h_2^2} \right) \\ + \frac{1}{h_3^2 h_1} \frac{\partial h_3}{\partial \eta} R + \frac{1}{h_3 h_1^2} \frac{\partial h_1}{\partial \eta} P = 0, \\ h_3 \frac{\partial}{\partial \xi} \left( \frac{T}{h_2 h_3^2} \right) + h_3 \frac{\partial}{\partial \eta} \left( \frac{S}{h_3^2 h_1} \right) + \frac{\partial}{\partial \zeta} \left( \frac{R}{h_1 h_2} \right) \\ + \frac{1}{h_1^2 h_2} \frac{\partial h_1}{\partial \zeta} P + \frac{1}{h_1 h_2^2} \frac{\partial h_2}{\partial \zeta} Q = 0, \end{aligned} \quad (1)$$

and I shall retain this notation throughout.

The solutions present themselves in two triads.

\* Communicated by the Author.

† Phil. Mag. July 1922, p. 274.

Taking as the starting-point

$$\begin{aligned} P &= \dots, & Q &= -h_3^2 \frac{\partial^2 \theta_1}{\partial \xi^2} \dots, & R &= -h_2^2 \frac{\partial^2 \theta_1}{\partial \eta^2} \dots, \\ S &= h_2 h_3 \frac{\partial^2 \theta_1}{\partial \eta \partial \xi} \dots, & T &= \dots, & U &= \dots, \end{aligned}$$

which satisfy the equations in third differential coefficients of  $\theta_1$ , and proceeding to satisfy the equations in the next lower degrees of differential coefficients, we find the expressions terminate. At this stage and in other stages throughout the paper we make use of the two triads of identities between the second differential coefficients of  $h$ 's and squares and products of first differential coefficients, which I shall cite as Lamé's Identities. I quote one identity from each triad:—

$$\begin{aligned} h_2 h_3 \frac{\partial^2 h_1}{\partial \eta \partial \xi} &= 2 \frac{h_2 h_3}{h_1} \frac{\partial h_1}{\partial \eta} \frac{\partial h_1}{\partial \xi} - h_3 \frac{\partial h_1}{\partial \eta} \frac{\partial h_2}{\partial \xi} - h_2 \frac{\partial h_1}{\partial \xi} \frac{\partial h_3}{\partial \eta}; \\ \frac{h_2^2}{h_3} \frac{\partial^2 h_3}{\partial \eta^2} + \frac{h_3^2}{h_2} \frac{\partial^2 h_2}{\partial \xi^2} &= 2 \frac{h_2^2}{h_3^2} \left( \frac{\partial h_3}{\partial \eta} \right)^2 + 2 \frac{h_3^2}{h_2^2} \left( \frac{\partial h_2}{\partial \xi} \right)^2 + \frac{h_1^2}{h_2 h_3} \frac{\partial h_2}{\partial \xi} \frac{\partial h_3}{\partial \xi} \\ &\quad - \frac{h_2}{h_3} \frac{\partial h_2}{\partial \eta} \frac{\partial h_3}{\partial \eta} - \frac{h_3}{h_2} \frac{\partial h_2}{\partial \xi} \frac{\partial h_3}{\partial \xi}. \end{aligned}$$

The final values for the elements of stress are:—

$$\begin{aligned} P &= 2 \frac{h_1^2}{h_2 h_3} \frac{\partial h_2}{\partial \xi} \frac{\partial h_3}{\partial \xi} \theta_1, \\ Q &= -h_3^2 \frac{\partial^2 \theta_1}{\partial \xi^2} - \frac{h_1^2}{h_3} \frac{\partial h_3}{\partial \xi} \frac{\partial \theta_1}{\partial \xi} + \frac{h_2^2}{h_3} \frac{\partial h_3}{\partial \eta} \frac{\partial \theta_1}{\partial \eta} \\ &\quad + \left( 2 \frac{h_3^2}{h_1} \frac{\partial h_1}{\partial \xi} - h_3 \frac{\partial h_3}{\partial \xi} \right) \frac{\partial \theta_1}{\partial \xi} \\ &\quad + 2 \left\{ \frac{h_2^2}{h_1} \frac{\partial^2 h_1}{\partial \xi^2} - \left( 2 \frac{h_3^2}{h_1^2} \frac{\partial h_1}{\partial \xi} - \frac{h_3}{h_1} \frac{\partial h_3}{\partial \xi} \right) \frac{\partial h_1}{\partial \xi} - \frac{h_2^2}{h_1 h_3} \frac{\partial h_1}{\partial \eta} \frac{\partial h_3}{\partial \eta} \right\} \theta_1, \\ R &= -h_2^2 \frac{\partial^2 \theta_1}{\partial \eta^2} - \frac{h_1^2}{h_2} \frac{\partial h_2}{\partial \xi} \frac{\partial \theta_1}{\partial \xi} + \left( 2 \frac{h_2^2}{h_1} \frac{\partial h_1}{\partial \eta} - h_2 \frac{\partial h_2}{\partial \eta} \right) \frac{\partial \theta_1}{\partial \eta} \\ &\quad + \frac{h_3^2}{h_2} \frac{\partial h_2}{\partial \xi} \frac{\partial \theta_1}{\partial \xi} \\ &\quad + 2 \left\{ \frac{h_2^2}{h_1} \frac{\partial^2 h_1}{\partial \eta^2} - \left( 2 \frac{h_2^2}{h_1^2} \frac{\partial h_1}{\partial \eta} - \frac{h_2}{h_1} \frac{\partial h_2}{\partial \eta} \right) \frac{\partial h_1}{\partial \eta} - \frac{h_3^2}{h_1 h_2} \frac{\partial h_1}{\partial \xi} \frac{\partial h_2}{\partial \xi} \right\} \theta_1, \end{aligned}$$

$$\begin{aligned}
S &= h_2 h_3 \frac{\partial^2 \theta_1}{\partial \eta \partial \xi} + h_1 h_3 \frac{\partial}{\partial \xi} \left( \frac{h_2}{h_1} \right) \frac{\partial \theta_1}{\partial \eta} + h_1 h_2 \frac{\partial}{\partial \eta} \left( \frac{h_3}{h_1} \right) \frac{\partial \theta_1}{\partial \xi}, \\
T &= \frac{h_1 h_3}{h_2} \frac{\partial h_2}{\partial \xi} \frac{\partial \theta_1}{\partial \xi}, \\
U &= \frac{h_1 h_2}{h_3} \frac{\partial h_3}{\partial \xi} \frac{\partial \theta_1}{\partial \eta}. \quad \dots \dots \dots (2)
\end{aligned}$$

By a concurrent cyclic interchange of the subscripts 1, 2, 3; of  $\xi, \eta, \zeta$ ; of P, Q, R; and of S, T, U and addition we complete the  $\theta$ -solution. To complete, for example, the value of P, we take one cyclic step forward from the value of R, and one such step retrograde from the value of Q.

To find a solution from the  $\psi$ -triad, we start from

$$\begin{aligned}
P &= 2h_2 h_3 \frac{\partial^2 \psi_1}{\partial \eta \partial \xi} \dots, \quad Q = \dots, \quad R = \dots, \\
S &= h_1^2 \frac{\partial^2 \psi_1}{\partial \xi^2} \dots, \quad T = -h_1 h_2 \frac{\partial^2 \psi_1}{\partial \xi \partial \eta} \dots, \\
U &= -h_1 h_3 \frac{\partial^2 \psi_1}{\partial \xi \partial \zeta} \dots,
\end{aligned}$$

and repeat the process as before.

The final values in this case are :—

$$\begin{aligned}
P &= 2h_2 h_3 \frac{\partial^2 \psi_1}{\partial \eta \partial \xi} - 2h_3 \frac{\partial h_2}{\partial \xi} \frac{\partial \psi_1}{\partial \eta} - 2h_2 \frac{\partial h_3}{\partial \eta} \frac{\partial \psi_1}{\partial \xi} \\
&\quad - 2 \left\{ h_3 \frac{\partial^2 h_2}{\partial \eta \partial \xi} + h_2 \frac{\partial^2 h_3}{\partial \eta \partial \xi} - \frac{h_3}{h_2} \frac{\partial h_2}{\partial \eta} \frac{\partial h_2}{\partial \xi} - \frac{h_2}{h_3} \frac{\partial h_3}{\partial \eta} \frac{\partial h_3}{\partial \xi} \right\} \psi_1, \\
Q &= -2 \frac{h_2 h_3}{h_1} \frac{\partial h_1}{\partial \eta} \frac{\partial \psi_1}{\partial \xi} + 2 \left\{ \frac{h_3}{h_1} \frac{\partial h_1}{\partial \eta} \frac{\partial h_2}{\partial \xi} + \frac{h_2}{h_1} \frac{\partial h_1}{\partial \xi} \frac{\partial h_3}{\partial \eta} \right\} \psi_1, \\
R &= -2 \frac{h_2 h_3}{h_1} \frac{\partial h_1}{\partial \xi} \frac{\partial \psi_1}{\partial \eta} + 2 \left\{ \frac{h_3}{h_1} \frac{\partial h_1}{\partial \eta} \frac{\partial h_2}{\partial \xi} + \frac{h_2}{h_1} \frac{\partial h_1}{\partial \xi} \frac{\partial h_3}{\partial \eta} \right\} \psi_1, \\
S &= h_1 h_2 h_3 \frac{\partial}{\partial \xi} \left( \frac{h_1}{h_2 h_3} \frac{\partial \psi_1}{\partial \xi} \right) \\
&\quad + \left\{ \frac{h_2^2}{h_1} \frac{\partial^2 h_1}{\partial \eta^2} + \frac{h_3^2}{h_1} \frac{\partial^2 h_1}{\partial \xi^2} - \frac{h_1^2}{h_2^2} \left( \frac{\partial h_2}{\partial \xi} \right)^2 \right. \\
&\quad \quad \quad + \frac{2h_1^2}{h_2 h_3} \frac{\partial h_2}{\partial \xi} \frac{\partial h_3}{\partial \xi} - \frac{h_1^2}{h_3^2} \left( \frac{\partial h_3}{\partial \xi} \right)^2 \\
&\quad \quad \quad + \frac{h_2}{h_1} \left( \frac{\partial h_2}{\partial \eta} + \frac{h_2}{h_3} \frac{\partial h_3}{\partial \eta} - 2 \frac{h_2}{h_1} \frac{\partial h_1}{\partial \eta} \right) \frac{\partial h_1}{\partial \eta} \\
&\quad \quad \quad \left. + \frac{h_3}{h_1} \left( \frac{\partial h_3}{\partial \xi} - 2 \frac{h_3}{h_1} \frac{\partial h_1}{\partial \xi} + \frac{h_3}{h_2} \frac{\partial h_2}{\partial \xi} \right) \frac{\partial h_1}{\partial \xi} \right\} \psi_1.
\end{aligned}$$

$$\begin{aligned}
T = & -h_1 h_2 \frac{\partial^2 \psi}{\partial \xi \partial \eta} - h_2 \left( \frac{\partial h_1}{\partial \eta} - 2 \frac{h_1}{h_3} \frac{\partial h_3}{\partial \eta} \right) \frac{\partial \psi_1}{\partial \xi} \\
& + h_1 \left( \frac{\partial h_2}{\partial \xi} - \frac{h_2}{h_3} \frac{\partial h_3}{\partial \xi} \right) \frac{\partial \psi_1}{\partial \eta} \\
& + h_1 \left\{ \frac{\partial^2 h_2}{\partial \xi \partial \eta} + \left( \frac{1}{h_1} \frac{\partial h_1}{\partial \eta} - \frac{1}{h_2} \frac{\partial h_2}{\partial \eta} - \frac{1}{h_3} \frac{\partial h_3}{\partial \eta} \right) \frac{\partial h_2}{\partial \xi} \right. \\
& \quad \left. + \frac{h_2}{h_3^2} \frac{\partial h_3}{\partial \eta} \frac{\partial h_3}{\partial \xi} \right\} \psi_1, \\
U = & -h_1 h_3 \frac{\partial^2 \psi_1}{\partial \xi \partial \zeta} - h_3 \left( \frac{\partial h_1}{\partial \zeta} - 2 \frac{h_1}{h_2} \frac{\partial h_2}{\partial \zeta} \right) \frac{\partial \psi_1}{\partial \xi} \\
& + h_1 \left( \frac{\partial h_3}{\partial \xi} - \frac{h_3}{h_2} \frac{\partial h_2}{\partial \xi} \right) \frac{\partial \psi_1}{\partial \zeta} \\
& + h_1 \left\{ \frac{\partial^2 h_3}{\partial \xi \partial \zeta} + \left( \frac{1}{h_1} \frac{\partial h_1}{\partial \zeta} - \frac{1}{h_2} \frac{\partial h_2}{\partial \zeta} - \frac{1}{h_3} \frac{\partial h_3}{\partial \zeta} \right) \frac{\partial h_3}{\partial \xi} \right. \\
& \quad \left. + \frac{h_3}{h_2^2} \frac{\partial h_2}{\partial \zeta} \frac{\partial h_2}{\partial \xi} \right\} \psi_1, \quad (3)
\end{aligned}$$

where again the triad may be completed by cyclic interchange.

Each of these solutions is a complete general solution of the stress-equations.

#### *First deduction.*

2. If we express the elements of any stress whatever according to the  $\theta$ -solution, and the elements of the reverse of that stress according to the  $\psi$ -solution, and add the two solutions, the sum of the expressions on the right in each of the six cases will be null.

Stating this result otherwise. If we add the  $\theta$ -solutions and  $\psi$ -solutions in full for each of the six elements of stress, there will be certain related values of  $\theta_1, \theta_2, \theta_3, \psi_1, \psi_2, \psi_3$  which will make the value of each element of stress zero.

Both by analogy with the results for Cartesians, and from general considerations, it will appear that the relations between  $\theta_1, \theta_2, \theta_3, \psi_1, \psi_2, \psi_3$  in this case are the same as those between  $e, f, g, a/2, b/2, c/2$ .

We therefore obtain the six identical relations between the

elements of strain, by writing the sum of the  $\theta$ -solutions, and the  $\psi$ -solutions in full, for each element of stress, and then replacing  $\theta_1$  by  $e$ ,  $\theta_2$  by  $f$ ,  $\theta_3$  by  $g$ ,  $\psi_1$  by  $a/2$ ,  $\psi_2$  by  $b/2$ ,  $\psi_3$  by  $c/2$ , and replacing each element of stress by zero.

The leading terms of the first and fourth of the set have the form

$$0 = -h_2^2 \frac{\partial^2 g}{\partial \eta^2} - h_3^2 \frac{\partial^2 f}{\partial \xi^2} + h_2 h_3 \frac{\partial^2 a}{\partial \eta \partial \xi} + \text{etc.},$$

$$0 = h_2 h_3 \frac{\partial^2 e}{\partial \eta \partial \xi} + \frac{1}{2} h_1^2 \frac{\partial^2 a}{\partial \xi^2} - \frac{1}{2} h_1 h_2 \frac{\partial^2 b}{\partial \xi \partial \eta} - \frac{1}{2} h_1 h_3 \frac{\partial^2 c}{\partial \xi \partial \zeta} + \text{etc.}$$

The complete expressions are lengthy, and require the expenditure of a little labour to obtain.

That the expressions on the right, expressed in terms of  $u$ ,  $v$ ,  $w$ , vanish identically may be verified to any desired extent, but the verification is really only of the accuracy of the work. It is certain that there is one set, and only one set, of identical relations between the differential coefficients of the elements of strain not exceeding the second degree.

An illustration, *ab initio*, in polar cylindrical coordinates is simple. The case of polar spherical coordinates is not much simpler than the general case.

### Second deduction.

3. To illustrate these six equations of identity, I proceed to find the six Elastic Stress Relations for this coordinate system.

In the first place, we must replace the elements of strain in these equations by their equivalents in terms of stress.

To explain the further processes, I shall suppose that, for the moment, the *inertia terms* are included in the stress-equations in the form  $\rho\ddot{u}$ ,  $\rho\ddot{v}$ ,  $\rho\ddot{w}$ . Then we must proceed to obtain from those equations the values of  $\rho\ddot{e}$ , etc.,  $\rho\ddot{f}$ , etc., after which these inertia terms may be omitted.

Then double the expression for  $\rho\ddot{e}$  and subtract the sum of the second and third of the six equations of identity. The details of the simplification are laborious and of little interest. There is again a triad of analogous relations from which we may verify that

$$\nabla^2(P + Q + R) = 0.$$



The final result for the first relation of the first triad is

$$\begin{aligned}
 & \nabla^2 P \\
 & + \frac{2m}{3m-n} \left\{ h_1 h_2 h_3 \frac{\partial}{\partial \xi} \left( \frac{h_1}{h_2 h_3} \frac{\partial}{\partial \xi} \right) + \frac{h_1^2}{h_2} \frac{\partial h_2}{\partial \xi} \frac{\partial}{\partial \xi} - \frac{h_2^2}{h_1} \frac{\partial h_1}{\partial \eta} \frac{\partial}{\partial \eta} \right. \\
 & \quad \left. + \frac{h_1^2}{h_3} \frac{\partial h_3}{\partial \xi} \frac{\partial}{\partial \xi} - \frac{h_3^2}{h_1} \frac{\partial h_1}{\partial \zeta} \frac{\partial}{\partial \zeta} \right\} (P+Q+R) \\
 & - 2 \left\{ \frac{h_1^2}{h_2^2} \left( \frac{\partial h_2}{\partial \xi} \right)^2 + \frac{h_2^2}{h_1^2} \left( \frac{\partial h_1}{\partial \eta} \right)^2 \right\} (P-Q) \\
 & \quad + 2 \left\{ \frac{h_1^2}{h_3^2} \left( \frac{\partial h_3}{\partial \xi} \right)^2 + \frac{h_3^2}{h_1^2} \left( \frac{\partial h_1}{\partial \zeta} \right)^2 \right\} (R-P) \\
 & + 2 \left\{ \frac{h_2 h_3}{h_1^2} \frac{\partial h_1}{\partial \eta} \frac{\partial h_1}{\partial \zeta} - \frac{h_2}{h_1} \frac{\partial h_1}{\partial \zeta} \frac{\partial h_3}{\partial \eta} - \frac{h_3}{h_1} \frac{\partial h_1}{\partial \eta} \frac{\partial h_2}{\partial \zeta} \right\} S \\
 & - 2 \left\{ 2h_3 \frac{\partial h_1}{\partial \zeta} \frac{\partial}{\partial \xi} - 2h_1 \frac{\partial h_3}{\partial \xi} \frac{\partial}{\partial \zeta} + \frac{h_1 h_3}{h_2^2} \frac{\partial h_2}{\partial \xi} \frac{\partial h_2}{\partial \zeta} \right. \\
 & \quad + h_3 \frac{\partial^2 h_1}{\partial \xi \partial \zeta} - h_1 \frac{\partial^2 h_3}{\partial \xi \partial \zeta} + \frac{h_1}{h_2} \frac{\partial h_2}{\partial \zeta} \frac{\partial h_3}{\partial \xi} - \frac{h_3}{h_2} \frac{\partial h_1}{\partial \zeta} \frac{\partial h_2}{\partial \xi} \\
 & \quad \left. + \frac{h_1}{h_3} \frac{\partial h_3}{\partial \xi} \frac{\partial h_3}{\partial \zeta} - \frac{h_3}{h_1} \frac{\partial h_1}{\partial \xi} \frac{\partial h_1}{\partial \zeta} \right\} T \\
 & - 2 \left\{ 2h_2 \frac{\partial h_1}{\partial \eta} \frac{\partial}{\partial \xi} - 2h_1 \frac{\partial h_2}{\partial \xi} \frac{\partial}{\partial \eta} + \frac{h_1 h_2}{h_3^2} \frac{\partial h_3}{\partial \xi} \frac{\partial h_3}{\partial \eta} \right. \\
 & \quad + h_2 \frac{\partial^2 h_1}{\partial \xi \partial \eta} - h_1 \frac{\partial^2 h_2}{\partial \xi \partial \eta} + \frac{h_1}{h_3} \frac{\partial h_2}{\partial \xi} \frac{\partial h_3}{\partial \eta} - \frac{h_2}{h_3} \frac{\partial h_1}{\partial \eta} \frac{\partial h_3}{\partial \xi} \\
 & \quad \left. + \frac{h_1}{h_2} \frac{\partial h_2}{\partial \xi} \frac{\partial h_2}{\partial \eta} - \frac{h_2}{h_1} \frac{\partial h_1}{\partial \xi} \frac{\partial h_1}{\partial \eta} \right\} U = 0. \quad (4)
 \end{aligned}$$

To form the first relation of the second triad, we add to the expression for  $\rho \ddot{a}$  the fourth of the six equations of identity, and find

$$\begin{aligned}
 & \nabla^2 S \\
 & + \frac{2m}{3m-n} \left\{ h_2 h_3 \frac{\partial^2}{\partial \eta \partial \zeta} + h_3 \frac{\partial h_2}{\partial \zeta} \frac{\partial}{\partial \eta} + h_2 \frac{\partial h_3}{\partial \eta} \frac{\partial}{\partial \zeta} \right\} (P+Q+R) \\
 & \quad + \frac{h_2 h_3}{h_1^2} \frac{\partial h_1}{\partial \eta} \frac{\partial h_1}{\partial \zeta} (2P-Q-R)
 \end{aligned}$$

$$\begin{aligned}
 & + \left\{ 2h_3 \frac{\partial h_2}{\partial \xi} \frac{\partial}{\partial \eta} - 2h_2 \frac{\partial h_3}{\partial \eta} \frac{\partial}{\partial \xi} + h_3 \frac{\partial^2 h_2}{\partial \eta \partial \xi} - h_2 \frac{\partial^2 h_3}{\partial \eta \partial \xi} \right. \\
 & \quad + \frac{h_2 \partial h_3}{h_3 \partial \eta} \frac{\partial h_3}{\partial \xi} - \frac{h_3 \partial h_2}{h_2 \partial \eta} \frac{\partial h_2}{\partial \xi} \\
 & \quad \left. + \frac{h_2 \partial h_1}{h_1 \partial \xi} \frac{\partial h_3}{\partial \eta} - \frac{h_3 \partial h_1}{h_1 \partial \eta} \frac{\partial h_2}{\partial \xi} \right\} (Q - R) \\
 & + \left\{ 4 \left\{ \frac{h_2^2}{h_3^2} \left( \frac{\partial h_3}{\partial \eta} \right)^2 + \frac{h_3^2}{h_2^2} \left( \frac{\partial h_2}{\partial \xi} \right)^2 \right\} \right. \\
 & \quad \left. - \left\{ \frac{h_1^2}{h_2^2} \left( \frac{\partial h_2}{\partial \xi} \right)^2 + \frac{h_2^2}{h_1^2} \left( \frac{\partial h_1}{\partial \eta} \right)^2 + \frac{h_1^2}{h_3^2} \left( \frac{\partial h_3}{\partial \xi} \right)^2 + \frac{h_3^2}{h_1^2} \left( \frac{\partial h_1}{\partial \eta} \right)^2 \right\} \right\} S \\
 & + \left\{ 2h_2 \frac{\partial h_1}{\partial \eta} \frac{\partial}{\partial \xi} - 2h_1 \frac{\partial h_2}{\partial \xi} \frac{\partial}{\partial \eta} - 3 \frac{h_1 h_2}{h_3^2} \frac{\partial h_3}{\partial \xi} \frac{\partial h_3}{\partial \eta} \right. \\
 & \quad + h_2 \frac{\partial^2 h_1}{\partial \xi \partial \eta} - h_1 \frac{\partial^2 h_2}{\partial \xi \partial \eta} + \frac{h_1 \partial h_2}{h_3 \partial \xi} \frac{\partial h_3}{\partial \eta} - \frac{h_2 \partial h_1}{h_3 \partial \eta} \frac{\partial h_3}{\partial \xi} \\
 & \quad \left. + \frac{h_1 \partial h_2}{h_2 \partial \xi} \frac{\partial h_2}{\partial \eta} - \frac{h_2 \partial h_1}{h_1 \partial \xi} \frac{\partial h_1}{\partial \eta} \right\} T \\
 & + \left\{ 2h_3 \frac{\partial h_1}{\partial \xi} \frac{\partial}{\partial \xi} - 2h_1 \frac{\partial h_3}{\partial \xi} \frac{\partial}{\partial \xi} - 3 \frac{h_1 h_3}{h_2^2} \frac{\partial h_2}{\partial \xi} \frac{\partial h_2}{\partial \xi} \right. \\
 & \quad + h_3 \frac{\partial^2 h_1}{\partial \xi \partial \xi} - h_1 \frac{\partial^2 h_3}{\partial \xi \partial \xi} + \frac{h_1 \partial h_2}{h_2 \partial \xi} \frac{\partial h_3}{\partial \xi} - \frac{h_3 \partial h_1}{h_2 \partial \xi} \frac{\partial h_2}{\partial \xi} \\
 & \quad \left. + \frac{h_1 \partial h_3}{h_3 \partial \xi} \frac{\partial h_3}{\partial \xi} - \frac{h_3 \partial h_1}{h_1 \partial \xi} \frac{\partial h_1}{\partial \xi} \right\} U = 0.
 \end{aligned}$$

### LIII. The Crystalline Structures of Silver Iodide.

By R. B. WILSEY\*.

IN a previous communication† giving the results of X-ray analyses of the crystal structures of the silver halides, the writer reported that silver iodide gave the diffraction pattern (powdered crystal) of the diamond cubic or "zinc-sulphide type" of structure. As stated then, crystals showing evidence of the hexagonal structure had not

\* Communication No. 184 from the Research Laboratory of the Eastman Kodak Company.

† R. B. Wilsey, *Phil. Mag.* xlii. p. 262 (1921).

been studied by the X-ray method. Refinements giving greater precision have been introduced in the experimental procedure, and the lattice constants of the silver halides have been re-measured; this time the hexagonal modification of silver iodide was included.

In examining the silver halides by the powder method, Davey\* also found the diamond type cubic structure for silver iodide. The diamond cubic structure of silver iodide has recently been questioned by Aminoff†, who states that within the usual experimental error the same lines of the powdered crystal diffraction pattern are given by either the hexagonal or diamond type cubic arrangement, and that the decision between these two structures must be made by other methods. With the aid of Laue diagrams and various crystallographic considerations, Aminoff concludes that the hexagonal structure is the correct structure for silver iodide, and reports the values  $a = 4.59 \text{ \AA}$ ,  $c = 7.73 \text{ \AA}$  for the edge and vertical axis respectively of the elementary hexagonal prism; these figures give the value 1.64 for the axial ratio.

In his "Survey of Existing Crystal Structure Data," Wyckoff‡ accepts Aminoff's conclusion, stating that incomplete observations of his own "had confirmed the truly hexagonal character of the salt." He points to the deduction of the cubic structure for silver iodide as "a very clear example of the dangers of trying to deduce crystal structures with unaided powder data," and he includes this case in his list of "well established examples" of "known failures to assign correct crystal structures"§.

There is much similarity between the two structures: in either one each atom of one kind is surrounded by four atoms of the other kind at the corners of a tetrahedron; and the atoms of each kind, taken alone, have a close-packed arrangement—in one case that of cubic close packing, and in the other that of hexagonal close packing. Either structure may be derived from the other by parallel shifts in the (111) planes of the cubic structure, or (0001) planes of the hexagonal structure.

A calculation of all the lines of a powdered crystal diffraction pattern to be expected from each structure shows

\* W. P. Davey, *Phys. Rev.* xix. p. 248 (1922).

† G. Aminoff, *Geol. Förh. Förh.* xlv. p. 444 (1922); abstracted in *Physik. Ber.* p. 827 (1922).

‡ R. W. G. Wyckoff, *J. Frank. Inst.* excv. p. 349 (1923).

§ R. W. G. Wyckoff, *J. Frank. Inst.* excv. p. 531 (1923).

that while the two structures have many lines in common, each has lines not possessed by the other, the hexagonal structure having much the greater number of lines characteristic of its own arrangement. Therefore the powdered crystal method should be able to distinguish between the two structures, provided satisfactory photographs can be obtained.

In the present experiments the samples of silver iodide were prepared from silver nitrate and potassium iodide, both of "reagent purity"; the possible impurities in the samples were small compared with the quantity of foreign substance required to show any effect upon the photograph.

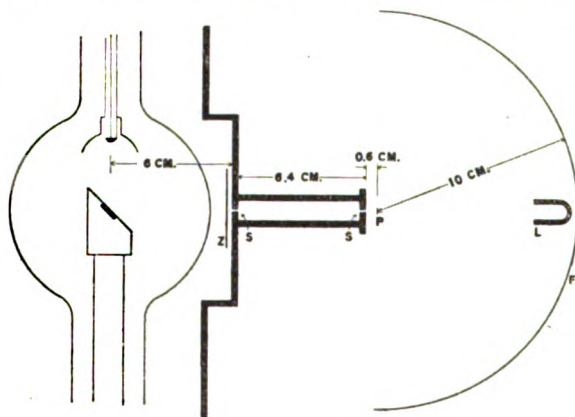
Considerable variation was found in the powder photographs of various samples of silver iodide, all of which were fully exposed under the same conditions. A few samples, including the one originally reported, showed only the lines of the diamond cubic structure, which includes two lines which cannot be accounted for by the hexagonal structure. The other samples varied from those showing one or two faint lines characteristic of the hexagonal structure to samples giving as many as ten such lines in addition to the seven lines common to both structures. All the photographs showing predominantly hexagonal structures contained one line which was most accurately accounted for by the cubic structure, differing from the nearest theoretical hexagonal line by an amount greater than experimental error. The conclusion is that both crystal forms exist, most of the samples showing a mixture of the two in which the hexagonal form predominates. The discrepancies in the results reported by different observers appear to be due to differences in the samples examined rather than in the methods of analysis used.

The accompanying diagram illustrates the experimental arrangement, and gives the essential dimensions of the apparatus. The Coolidge tube with molybdenum target was operated at 30 kv. (effective), and the  $K\alpha$  line was isolated with the aid of the zirconium oxide filter Z. The slits S were each 0.4 millimetre wide. A U-shaped piece of lead, L, protected the film from the primary X-ray beam during most of the exposure, and thereby avoided the fogging action of the secondary radiation which would be produced where the primary beam meets the film and cassette. The crystal powder was made into a thin paste with a cellulose varnish and coated upon a thin ribbon of celluloid; when

dry the powdered layer was approximately 0.2 millimetre thick and 2 millimetres wide. The sample was centered in the axis of the spectrometer with the aid of a telescope and crosshair. An exposure of 120 to 150 milliampere hours was usually sufficient to give a well-exposed film.

The error due to shrinkage of the film during the development process was avoided in the following way:—

Equally spaced notches were cut in the semicircular cassette at approximately 10 degrees apart, and during the exposure these notches were printed on the film by the general scattered radiation. The distances apart of the lines of the diffraction pattern were referred to the spacing of the images of the notches. The final calibration of the spacing of the notches was carried out by a series of powder



photographs of sodium chloride, so that the lattice constants here reported are based on the accepted value of  $2.814 \times 10^{-8}$  cm. for the spacing of the (100) planes of sodium chloride. As a rule the lattice constant determined from a single film did not differ by more than  $1/8$  per cent. from the mean value of several films; hence the ratio of any lattice constant to that of sodium chloride should be correct to within  $1/4$  per cent.

Duane's\* values for the wave-length of the  $K\alpha$  doublet of molybdenum are  $0.70783 \times 10^{-8}$  cm. and  $0.71212 \times 10^{-8}$  cm. for  $\alpha_1$  and  $\alpha_2$  respectively,  $\alpha_1$  having double the intensity of  $\alpha_2$ . The weighted mean value  $0.7093 \times 10^{-8}$  cm. was taken as the wave-length of the  $K\alpha$  radiation in the present experiments.

\* W. Duane, Bull. Nat. Res. Council, vol. i. No. 6, p. 383 (1920).

The angular deviation of each line was determined from the distance apart of its two reflexions on either side of the primary beam, and this value was checked by a measurement of the distances of the lines from the undeviated image of the slit.

A set of data showing the cubic form (zinc-sulphide arrangement) of silver iodide is given in Table I. The first five columns refer to the theoretically computed lines for this structure, and the last four columns refer to the observed data.

TABLE I.

Indices of Form.	No. of Co-operating Planes N.	Phase Factor F.	$N \times F$ .	Relative Spacing of Planes, Theoretical $d/a$ .	Observed Angular Deviation $2\theta$ .	Observed Spacing of Planes $d$ in Ångströms.	Side of Elementary Cube in Ångströms.	Estimated Intensity of Line.
111	4	0.5	2	.5774	10 51	3.749	6.493	10
220	6	1.0	6	.3536	{ *15 49 17 48	2.294 2.292	6.487 6.480	1 8
311	12	0.5	6	.3014	20 53	1.957	6.493	7
400	3	1.0	3	.2500	25 15	1.623	6.492	1
331	12	0.5	6	.2294	27 35	1.488	6.486	3
422	12	1.0	12	.2041	31 5	1.324	6.485	3
511	12	0.5	6	.1924	33 1	1.248	6.485	2
333	4	0.5	2	} 8				
440	6	1.0	6		36 1	1.147	6.490	1
531	24	0.5	12	.1690	37 43	1.097	6.492	1.5
Mean ...							6.488	

\* Reflexion of  $\beta$  line,  $\lambda = 0.6311 \times 10^{-8}$  cm.

The phase factor,  $F$ , of each set of planes, given in column 3, is defined by Hull† as the “ratio of the square of the sum of the amplitudes of reflexion from all the planes added as vectors to the square of their algebraic sum.” In computing phase factors, the amplitude of reflexion was taken proportional to atomic number. In the cases where reflexions from planes of silver atoms differ in phase by  $180^\circ$  from reflexions from planes of iodine atoms, the phase factor is negligible and is not recorded; no lines corresponding to such reflexions were found. The product  $N \times F$  gives the relative intensity to be expected of neighbouring lines, provided allowance is made for the decrease of scattering

† A. W. Hull, Phys. Rev. xvii. p. 571 (1921).

power with increasing angle of deviation. Since this function is not known for silver iodide, only a rough correspondence is to be expected between the values of  $N \times F$  and the estimated intensities of the lines.

Column 5 gives the theoretical ratio of  $d$  (the spacing of the planes) to  $a$  (the side of the elementary cube). The observed spacing of the planes is computed from the observed angular deviation by the Bragg relation  $n\lambda = 2d \sin \theta$ . The value of the side of the elementary cube is computed for each reflexion by dividing the observed spacing by the theoretical value of  $\frac{d}{a}$ . The substantial agreement of the various cube side values shows how closely each reflexion fits the assumed structure.

Within the range of angles where lines are observable, all the lines required for the diamond cubic structure and none others are present. Two of the lines, the (400) and the (331) reflexions, cannot be accounted for by the hexagonal structure; the (400) line is not near any line of the hexagonal pattern; the theoretical (331) spacing differs from the nearest hexagonal spacing ( $21\bar{3}0$ ) by 0.9 per cent. In the above table the observed (331) line gives a cube side value differing by less than 0.1 per cent. from the mean, thus showing its preference for the cubic lattice. In six powder photographs of various samples of cubic silver iodide, the maximum observed deviation of the (331) cube side value from the mean for the given film was  $1/4$  per cent., and the average deviation  $1/8$  per cent. The average cube side for the six exposures was  $6.493 \times 10^{-8}$  cm. Two of these films showed no other lines than those of the diamond cubic structure; the other four each had one faint line ( $10\bar{1}0$ ) belonging only to the hexagonal structure, showing that these samples contained a small proportion of the hexagonal form.

Most of the samples of silver iodide examined showed predominantly the hexagonal structure. Table II. gives a representative set of data obtained from such a sample. If the tetrahedra of the hexagonal structure are equilateral, as are those of the cubic structure, the axial ratio should be 1.633, that of the hexagonal close packing of equal spheres; this value is assumed in the calculations. The positions of the atoms in this structure are:—

Silver	$\begin{cases} m \\ m + 1/3 \end{cases}$	$\begin{cases} n \\ n + 2/3 \end{cases}$	$\begin{cases} pc, \\ (p + 1/2)c, \end{cases}$
Iodine	$\begin{cases} m + 1/3 \\ m \end{cases}$	$\begin{cases} n + 2/3 \\ n \end{cases}$	$\begin{cases} (p + 1/8)c, \\ (p + 5/8)c, \end{cases}$

where  $m$ ,  $n$ , and  $p$  have all possible integral values.

This pattern shows one line which fits the cubic (331) spacing much more closely than it does the nearest hexagonal spacing (21 $\bar{3}$ 0) indicating the presence of the cubic crystal form. The data on this line will be considered more fully in a later paragraph.

TABLE II.

Indices of Form.	No. of Co-operating Planes N.	Phase Factor F.	N X F.	Relative Spacing of Planes, Theoretical $d/a$ .	Observed Angular Deviation $2\theta$ .	Observed Spacing of Planes $d$ in Ångströms.	Side of Elementary Hexagon in Ångströms.	Estimated Intensity of Line.
10 $\bar{1}$ 0	3	.25	.75	.8662	10 12	3.991	4.607	7
0002	1	.50	.50	.8165	10 53	3.742	4.583	7
10 $\bar{1}$ 1	6	.112	.67	.7651	11 35	3.512	4.591	3
10 $\bar{1}$ 2	6	.126	.76	.5941	14 54	2.786	4.606	2
11 $\bar{2}$ 0	3	1.00	3.00	.5000	{ *15 50 17 46	2.291 2.296	4.582 4.592	1 10
10 $\bar{1}$ 3	6	.184	1.10	.4608	19 18	2.115	4.590	6
20 $\bar{2}$ 0	3	.25	.75	.4331				
11 $\bar{2}$ 2	6	.50	3.00	.4264	20 49	1.963	4.604	8
20 $\bar{2}$ 1	6	.112	.67	.4185				
20 $\bar{2}$ 2	6	.141	.85	.3826				
20 $\bar{2}$ 3	6	.641	3.85	.3389	26 19	1.558	4.598	2
21 $\bar{3}$ 0	6	.250	1.50	.3272				
331	12	(cubic)	...	...	27 31	1.492	...	1
21 $\bar{3}$ 1	12	.026	.31	.3209				
10 $\bar{1}$ 5	6	.641	3.85	.3056	29 13	1.406	4.602	1
21 $\bar{3}$ 2	12	.126	1.51	.3038				
30 $\bar{3}$ 0	3	1.00	3.00	.2887	31 4	1.324	4.587	1
21 $\bar{3}$ 3	12	.64	7.68	.2805	31 59	1.287	4.590	1
30 $\bar{3}$ 2	6	1.00	6.00	.2722	33 00	1.248	4.586	1
0003	1	.50	.50	.2722				
20 $\bar{2}$ 5	6	.64	3.84	.2607	34 33	1.195	4.582	0.7
10 $\bar{1}$ 6	6	.125	.75	.2596				
22 $\bar{4}$ 0	3	1.00	3.00	.2500	36 00	1.148	4.591	0.4
31 $\bar{4}$ 0	6	.25	1.50	.2402				
11 $\bar{2}$ 6	6	.50	3.0	.2390	37 42	1.097	4.591	1
31 $\bar{4}$ 1	12	.113	1.37	.2376	39 4	1.061	4.603	0.5
20 $\bar{2}$ 6	6	.126	.76	.2304				
31 $\bar{4}$ 2	12	.126	1.51	.2304				

Mean ... 4.593

\* = Reflexion of  $\beta$  line.



The mean value of the side of the hexagonal prism, taken from nine exposures on various samples, was  $4.593 \times 10^{-8}$  cm.

The data do not afford a very precise direct determination of the axial ratio. The only line giving an independent measurement of the height of the elementary hexagonal prism is the second-order reflexion from the (0001) plane; the small angular deviation of this line gives a relatively low precision in the value of the planar spacing. Independent measurements of the side of the hexagon are given by four reflexions ( $10\bar{1}0$ ), ( $11\bar{2}0$ ), ( $20\bar{2}0$ ) and  $22\bar{4}0$ ). The mean value of the axial ratio, as determined from these reflexions in the nine exposures, was  $1.633 \pm .008$ .

Table III. gives the complete data on the line designated as (331) in Table II., showing how this fits the two nearest hexagonal spacings as compared with the cubic (331) spacing. The cubic (331) spacing lies nearly midway between the hexagonal ( $21\bar{3}0$ ) and ( $21\bar{3}1$ ) spacings; the reflexion from the ( $21\bar{3}1$ ) plane would hardly be expected to appear on account of its low value of the product  $N \times F$ . In Table III. the edge of the elementary tetrahedron is computed from the position of the observed line, assuming it to be reflected from each of the three planes in turn, and these values are compared with the mean value of the tetrahedral edge for the given film. In every case the observed line fits the (331) spacing much more closely than either of the nearest hexagonal spacings.

The evidence appears quite conclusive that every sample of silver iodide studied contained the cubic form; in a few cases none but the cubic structure was evident; in some, one or two faint lines were present which belonged only to the hexagonal form; while in most of the samples the hexagonal form predominated. No systematic study was made of the conditions governing the production of one crystal form or the other; the first sample showing the cubic form was prepared by precipitation; the other cubic crystals were produced by fusion of the salt and quenching in cold water; as a rule, the predominantly hexagonal form was produced by every method tried, whether precipitation or the quenching or slow cooling of a fused sample.

The lattice constants of silver chloride and silver bromide were also re-determined. Silver chloride gave the lines of a face-centered cubic structure in which the reflexions from planes of all odd indices were of lower intensity than would be expected from such a structure composed of like atoms; this effect would be expected in a structure of the sodium chloride type where the two kinds of atoms differ considerably

in atomic number. The mean value of  $d(100)$  from four exposures was  $2.770 \times 10^{-8}$  cm.

TABLE III.

Film No.	Observed Angular Deviation 2 $\theta$ .	Observed Spacing of Planes in Angströms.	Mean Tetrahedral Edge or Hexagonal Side for each Film.	Tetrahedral Edge computed from observed line.	Differences.	Assumed Planes Indices of Form.
1 .....	27 36.4	1.486	4.587	4.542 4.582 4.632	-0.045 -0.005 +0.045	21 $\bar{3}$ 0 331 21 $\bar{3}$ 1
2 .....	27 33.6	1.489	4.588	4.550 4.589 4.639	-0.038 +0.001 +0.051	21 $\bar{3}$ 0 331 21 $\bar{3}$ 1
3 .....	27 36	1.487	4.595	4.543 4.583 4.633	-0.052 -0.012 +0.038	21 $\bar{3}$ 0 331 21 $\bar{3}$ 1
4 .....	27 29.2	1.493	4.597	4.562 4.601 4.651	-0.035 +0.004 +0.054	21 $\bar{3}$ 0 331 21 $\bar{3}$ 1
5 .....	27 27.2	1.495	4.597	4.567 4.607 4.657	-0.030 +0.010 +0.060	21 $\bar{3}$ 0 331 21 $\bar{3}$ 1
6 .....	27 28.4	1.494	4.593	4.524 4.603 4.654	-0.069 +0.010 +0.061	21 $\bar{3}$ 0 331 21 $\bar{3}$ 1
7 .....	27 31.4	1.491	4.591	4.556 4.595 4.645	-0.035 +0.004 +0.054	21 $\bar{3}$ 0 331 21 $\bar{3}$ 1
8 .....	27 30.6	1.492	4.593	4.558 4.597 4.648	-0.035 +0.004 +0.055	21 $\bar{3}$ 0 331 21 $\bar{3}$ 1
9 .....	27 28.2	1.494	4.595	4.564 4.604 4.654	-0.031 +0.009 +0.059	21 $\bar{3}$ 0 331 21 $\bar{3}$ 1
Mean ...			4.593			

Silver bromide gave the diffraction pattern of a simple cubic lattice. This pattern is accounted for by the sodium chloride type of structure where the two kinds of atoms are of sufficiently similar atomic numbers as to act as

similar diffracting centres. The mean value of  $d$  (100) from four films was  $2.884 \times 10^{-8}$  cm.

The deduction of the sodium chloride structure for both silver chloride and silver bromide follows simply from the published methods of analysis of powdered crystal diffraction patterns. The possibility that either of these simple compounds has any other structure seems so remote that it is considered superfluous to publish the data in detail.

Several samples of metallic silver of known high purity were also examined by the powder method; this substance gave photographs having unusually well-defined lines. The pattern was that of a face-centred cubic structure, as has been reported by other investigators\*; the mean value of the side of the elementary cube from six exposures was  $4.078 \times 10^{-8}$  cm. Very good diffraction photographs were also obtained from the blackened silver of a developed photographic film.

The lattice constants of the structures studied are summarized in Table IV.

Crystal.	Lattice Structure.	Side of Elementary Unit of Structure in Ångströms.	Distance apart of nearest Atomic Centres in Ångströms.
Silver chloride .....	Simple cubic, NaCl type.	5.540	2.770
Silver bromide .....	Simple cubic, NaCl type.	5.768	2.884
Silver iodide .....	Diamond cubic ZnS type.	6.493	2.812
Silver iodide .....	Hexagonal, ZnO type.	4.593 ( $c/a = 1.633$ )	2.813
Metallic silver .....	Face-centred cubic.	4.078	2.884

In conclusion, it may be pointed out that while the X-ray powder method of crystal analysis has its limitations, as have other methods, it has also its advantages. The great majority of crystalline substances do not ordinarily occur in large crystals, and the powder method is the only method applicable to crystals as they exist in a finely divided state. The convenience with which it may be used to examine a large number of samples prepared in various ways has made it possible in the present case to obtain more complete information about the crystalline characteristics of silver iodide than has been obtained by other methods depending upon single large crystals.

Rochester, N.Y.,  
May 8, 1923.

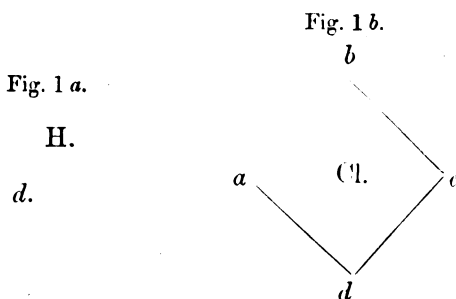
\* L. Vegard, *Phil. Mag.*, **xxi**. p. 83 (1916). L. W. McKeehan, *Phys. Rev.* **xx**. p. 424 (1922).

LIV. *Studies in the Electron Theory of Chemistry. On the changes in chemical properties produced by the substitution of one element or radicle by another, with applications to benzene substitutions.* By Sir J. J. THOMSON, O.M., F.R.S., Master of Trinity College, Cambridge\*.

WHEN a monovalent atom or radicle—such as F, Cl, Br, I, OH, CH<sub>3</sub>, CN—is substituted for an atom of hydrogen the number of electrons is increased; these additional electrons, together with the corresponding positive charges, will change the electric field in and around the molecule. It is the object of this paper to investigate the nature of this change and the effect it might be expected to have on the chemical properties of the molecule.

I will begin with a case which I have already discussed to some extent in my lectures on "The Electron in Chemistry," given at the Franklin Institute, Philadelphia (Journal of the Franklin Institute, June 1923), that of the replacement of hydrogen by halogens. As the halogen atom has seven electrons in the outer layer, while the hydrogen atom has only one, there will be six more disposal electrons after the halogen atom has been introduced, the negative charges on these will be balanced by the excess of six units of positive charge which the positive core of the halogen atom has over that of the hydrogen one.

The dispositions of the electrons before and after the substitution are represented in figs. 1 a, b. H, fig. 1 a, is the

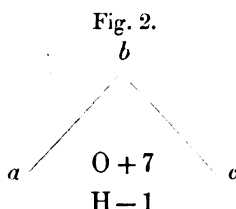


positive core of the hydrogen atom, *d* the projection on the plane of the paper of the line joining the two electrons which bind it to the rest of the molecule. Cl, fig. 1 b, is the positive core of the chlorine atom, *a*, *b*, *c*, *d* the projections of the sides

\* Communicated by the Author.

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of the octet which surround this core, each side corresponds to two electrons. The difference in the electric field produced by substitution will be that due to the system represented in fig. 2, where again  $a$ ,  $b$ ,  $c$  represent the projections of three



sides of the octet, each side corresponding to two electrons, O represents the positive nucleus of the halogen atom with a charge 7; the negative charge  $-1$  at H, where H is the position of the nucleus of the hydrogen atom which has been displaced, represents the effect of removing the positive part of the hydrogen atom. The four electrons at  $a$  and  $c$  together with the positive charge  $+7$  at O are approximately equivalent to a charge  $+3$  at O, and the whole system is equivalent to charges  $-1$  at H,  $+3$  at O and  $-2$  at  $b$ . The  $-2$  at  $b$  together with a charge  $+2$  at O are equivalent to an electrostatic doublet whose moment is  $2e \times Ob$ , where  $e$  is the charge on an electron; the  $-1$  at H and the  $+1$  which is left over from O are equivalent to a doublet whose moment is  $e \times OH$ , the axis of this doublet is in the opposite direction to that of the previous one, the moment of the resultant doublet is equal to

$$e(2Ob - OH);$$

now

$$OH = Od - Hd = Ob - Hd,$$

hence the moment of the resultant doublet is equal to

$$e(Ob + Hd)$$

$$= es,$$

where  $s$  is the sum of the radii of the hydrogen and halogen atoms. The orientation of this doublet is the same as that of one with negative electricity on the halogen atom and positive on the one with which it is combined. Thus, for example, if we replace one of the hydrogen atoms in marsh gas by chlorine the molecule of  $\text{CH}_3\text{Cl}$  would have an electrostatic moment whose sign would be the same as that of an electric doublet with positive electricity on the carbon atom and negative on the chlorine one. The magnitude of the moment would be  $e$  times the sum of the radii of the

hydrogen and chlorine atoms, *i. e.*, it would not differ much from the electric moment of a molecule of HCl.

Let us now take the case of the replacement of H by OH. The fact that the water molecule has a considerable electrostatic moment shows that it cannot be represented by a symmetrical arrangement such as a cubical octet of electrons surrounding the positive core of an oxygen atom with the positive cores of two hydrogen atoms symmetrically placed outside. If one of the hydrogen atoms were to go inside the octet of electrons the water molecule could have a finite moment. We shall suppose, therefore, that the radicle OH consists of seven electrons arranged round the positive cores of atoms of hydrogen and oxygen. The problem is now practically the same as that of the chlorine atom and we see that the effect of replacement of H by OH will introduce a moment whose sign is the same as that of an electric doublet with negative electricity on (OH) and positive on the atom with which it is combined; the magnitude of the moment is  $cs$ , where  $s$  is the sum of the radii of an atom of hydrogen and of a negatively charged OH radicle. This is also the moment of a water molecule approximately. Hence we see that the effect of replacing H by OH is to introduce into the molecule an electrostatic moment equal to that of a water molecule. Thus if we replace one of the hydrogens in  $\text{CH}_4$  by OH, producing a molecule of methyl alcohol, the electrostatic moment of a molecule of methyl alcohol ought to be much the same as that of a molecule of water. Now the presence of electrostatic moments gives rise to abnormally large specific inductive capacities, and substances such as water and methyl alcohol, which have very large specific inductive capacities, owe them to the presence of electrostatic moment in their molecules, and the measure of the capacity is a measure of the moment. We have been led to the result that the moment of a molecule of water ought not to differ much from that of one of alcohol. Hence, if this result is true, the specific inductive capacities of water and methyl alcohol *estimated for the same number of molecules* ought not to be very different. This is in agreement with the results of experiments, for the specific inductive capacities in the liquid state of water  $\text{H}_2\text{O}$ , methyl alcohol  $\text{CH}_3\text{OH}$ , ethyl alcohol  $\text{C}_2\text{H}_5\text{O}$ , propyl alcohol  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$  are in the proportion of 80:79:84:85. The specific inductive capacities are estimated for the same number of molecules. The value of the specific inductive capacity shows a tendency to rise as the complexity of the molecule increases, this is what we should expect as the intense electric field due to the

moment will give rise by induction on the rest of the molecule to moments of the same sign as the original moment, and thus the value of the moment of the whole molecule will be greater than that introduced by the substituent.

If we apply the same considerations to the substitutions of  $\text{NH}_2$  for H, we find that it introduces a moment whose negative end is towards the  $\text{NH}_2$  and positive end towards the atom with which it is combined and whose magnitude is  $es$ , where  $s$  is the sum of the radii of an atom of hydrogen and a negatively charged radicle  $\text{NH}_2$ .

Another way of treating the problem is to notice that the electrical effect produced by a number of movable electrical charges when acted upon by an electric field is much the same as that of a conductor of electricity such as a metallic sphere filling the volume through which the charges are distributed. When such a collection of charges is acted upon by an electric field the charges will be displaced so that the force called into play by this displacement on any one of the charges is just sufficient to balance the force on that charge due to the external electric field. If we expose a metallic sphere to this field there will be a displacement of the electricity on the sphere, the negative moving in the opposite direction to the electric force, the positive in the same direction; the tangential force due to this displacement balances at any charge on the surface of the sphere the tangential force on the same charge due to the external electric field. Thus the effect of the displacement of a number of mobile charged bodies is much the same as that of the displacement of the electrification on a metallic sphere. An illustration of this is afforded by the Electron Theory of Specific Inductive Capacity, which shows that the electrostatic moment of a group of a considerable number of electrons with the corresponding positive charge is proportional to that which would be induced in a metallic sphere occupying the volume through which the charges are distributed.

Thus we may take as an approximation to the electrical effect produced by an atom or radicle with no intrinsic moment that which would be produced by a conducting sphere of the same radius; for the analogy to hold the radicle or atom must be able to receive a negative charge, so that the octet of electrons must not be complete.

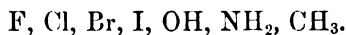
We shall illustrate the use of this method by applying it to the case of the replacement of hydrogen by chlorine. Let us suppose that P is the electron in the parent substance which links it to the chlorine atom in one case and to the hydrogen atom in the other. What will be the effect of

bringing an uncharged metal sphere up to P? The sphere will receive the charge on the electron and become negatively charged. The electrical effect of this negatively charged sphere would to a first approximation be the same as if the negative charge were placed at C, the centre of the sphere. Thus the electrical effect of the introduction of the sphere is to move the electron from P to C. This is equivalent to leaving the electron where it was and introducing an electric doublet whose moment is  $e \times PC$  and whose positive end is towards P and negative one towards C. Since the chlorine atom has only seven electrons in the outer layer it can receive another electron and will produce an effect similar to that of the sphere.

Now consider the effect of introducing an atom of hydrogen instead of one of chlorine. The hydrogen atom has an electrostatic moment of its own equal to  $er$ , where  $r$  is the radius of the atom, and it carries this or, at any rate, a large component of it into combination. The positive part of this electrostatic doublet is away from P while the negative end is towards it; thus the moment is of the opposite sign to that due to the introduction of the chlorine atom. Hence the change produced by the substitution of the chlorine atom for a hydrogen one is equivalent to the introduction of an electrostatic moment equal to  $e(PC + r)$ , i. e.,  $e$  (sum of the radii of the chlorine and hydrogen atoms), the positive end of this moment is next the atom with which the chlorine combines, the negative end towards the chlorine; this is the same result as we got by the use of the other method.

We see from this result that whenever we introduce an atom or radicle which has no intrinsic moment and which can receive an additional electron, i. e., one which contains an uncompleted octet, the effect will be represented by an electrostatic doublet whose negative end is on the side of the radicle and the positive end on the side of the molecule with which the radicle combines.

Examples of atoms and radicles of this type are—



Each of these has seven disposable electrons.

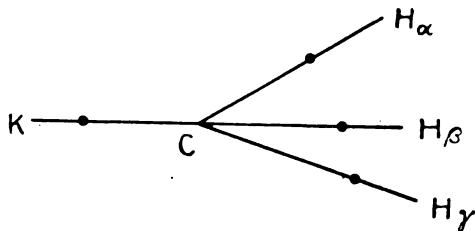
The radicle  $\text{CH}_3$  requires special consideration, for in some cases the substitution of this for hydrogen seems to produce a change in the moment, in other cases it does not. Thus in  $\text{H.OH}$ ,  $\text{CH}_3.\text{OH}$ ,  $\text{CH}_3\text{CH}_2\text{OH}$ , each molecule may be derived from the preceding by substituting  $\text{CH}_3$  for H.



The specific inductive capacities per molecule of these substances are practically the same, so that the substitution of  $\text{CH}_3$  for  $\text{H}$  has produced at most a very small change in the moment. On the other hand, when  $\text{H}$  in formic acid is replaced by  $\text{CH}_3$ , as in acetic acid, a very large diminution in the specific inductive capacity is produced. Again, when one of the hydrogens in benzene is, as in toluene, replaced by  $\text{CH}_3$ , the change in moment must be small as the specific inductive capacity of toluene is normal.

When an atom of hydrogen in a molecule of hydrogen with no moment is replaced by  $\text{CH}_3$  a molecule of  $\text{CH}_4$ , which has also no moment, is produced. Thus when  $\text{CH}_3$  replaces an atom of hydrogen  $\text{H}_1$  no moment is produced when  $\text{H}_1$  is in combination with another atom of hydrogen. It might, however, happen that if  $\text{H}_1$  was combined with something different from hydrogen a finite moment would be produced. For when  $\text{H}_1$  is combined with  $\text{K}$  the configuration after the replacement of  $\text{H}$  is represented in fig. 3,

Fig. 3.



where  $\text{K}$  is the atom which was in combination with  $\text{H}$ , before the replacement,  $\text{H}_\alpha, \text{H}_\beta, \text{H}_\gamma$ , the hydrogen atoms in  $\text{CH}_3$ . The electrical moment will depend on the angles  $\text{CH}_\alpha, \text{CH}_\beta, \text{CH}_\gamma$  make with each other; if these lines close up and get more nearly in a straight line, the moment due to this part of the system, which has the positive side towards  $\text{C}$  and the negative towards  $\text{H}_\alpha, \text{H}_\beta, \text{H}_\gamma$ , will increase. The positions of  $\text{CH}_\alpha, \text{CH}_\beta, \text{CH}_\gamma$  will depend upon the positive charge at  $\text{K}$ . The system  $\text{CH}_\alpha$  consists of a positive ion and two electrons attached to  $\text{C}$ . The positive charge at  $\text{K}$  will make  $\text{CH}_\alpha$  move as if it attracted it; if  $\text{K}$  is moved further away the lines  $\text{CH}_\alpha, \text{CH}_\beta, \text{CH}_\gamma$  will make smaller angles with each other and the system will have a moment with the positive end towards  $\text{C}$  and the negative end to the right. If  $\text{K}$  were a more complex system than a hydrogen atom, say a hydrocarbon with a positive charge, the equivalent of

this positive charge might be further from the octet of electrons round C than it would if K were hydrogen, because the distance of hydrogen from the octet is equal to the distance of the electron in a hydrogen atom from the core, which is about the minimum distance of a positive charge from an electron; thus the replacement of H by CH<sub>3</sub> may introduce a moment, whose magnitude will depend upon the system with which CH<sub>3</sub> is in combination.

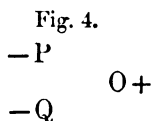
It must be remembered, too, that the measurement of the specific inductive capacity only gives us the resultant moment; which represents the action of the system at large distances, within the molecule itself large forces might be produced by distributions of electricity which have no finite moment.



Thus, for example, if there are positive unit charges at B and D and a negative charge  $-2$  at C, the point midway between B and D, these constitute a system with no resultant moment, yet its effect at a point A, whose distance from B is comparable with BC, will be a considerable fraction of that due to a charge 1 at B and  $-1$  at C, a system which has a finite moment. Thus in considering the effect produced by substitution on the electric field in the immediate neighbourhood of the substituted atom, the most important electrical effects are those which take place quite close to the atom.

Thus let P be the electron in the parent substance which binds the hydrogen atom before substitution and the substituted atom or radicle afterwards, to the parent molecule. Let us consider how the field due to P is modified when (1) it binds an atom of hydrogen, (2) when it binds an atom of a substituent.

When an atom of hydrogen is bound, an electron Q of this atom comes nearer to P than the positive hydrogen ion O, forming a system like fig. 4; to the left of P the



force due to the electron Q will overbalance that due to the ion O, so that the effect of the hydrogen will be of the same sign as that which would in the absence of the hydrogen be produced by an increase in the negative charge at P.

Now suppose that instead of combining with hydrogen the molecule combines with a substituent for hydrogen. If among the atoms that make up the substituent there is one that has not got a complete octet, P may join up with this; this, as we have seen, from the analogy with the metal sphere, has much the same effect as removing P to the centre of this atom; thus a combination with a substituent of this kind will produce a change in the electrical field of the same sign as that which would be produced by a diminution of the electrical charge on P, or what is equivalent, by the introduction of an electrical doublet with its positive side towards the parent system. For places close to P this change will determine the nature of the change in the electrical forces, even though in other parts of the substituent there may be distributions of electrons and positive charges which introduce moments of opposite sign to these, and which may reverse the resultant moment, without reversing the sign of the effect near P. The case of  $\text{CH}_3$  is one in point; here we have 7 electrons round the carbon atom, forming a system of the kind we have contemplated, when P completes the octet, the effect is to introduce a doublet with its positive side towards the parent system; the hydrogen atoms in  $\text{CH}_3$  may be regarded as introducing a doublet of opposite sign, but this doublet is further away from P than the other and so cannot neutralize its effect at P, though it might do so further away.

In this case the removal of hydrogen and the introduction of the substituent both produce effects of the same sign and are equivalent to the introduction of an electric doublet with its positive part towards the molecule with which the hydrogen was combined. This result will be true for all substituents which contain an uncompleted octet such as Cl, OH,  $\text{CH}_3$ ,  $\text{NH}_2$ .

There may be substituents, however, of another type, where, as in the hydrogen atom, we have a detached electron and some distance from it a unit positive charge.

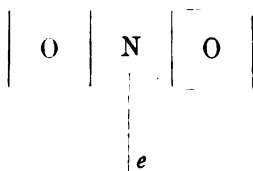
When this substituent enters the parent molecule, it, like the hydrogen atom, produces an electric field whose sign is the same as that which would be produced by an increase in the negative charge on P. If this effect is greater than the corresponding one for hydrogen, then the result of substitution will be of the same sign as that due to the introduction of a doublet whose negative end is towards the parent molecule. If, on the other hand, the effect of the substituent is less than that of hydrogen, substitution will produce an effect of the same sign as that due to chlorine.

Substituents with a detached electron and a positive ion will have a finite electrical moment, the greater this moment the greater will be the distance of the positive ion from the two electrons which couple it with the molecule with which it combines. The positive ion produces an electric field of the same sign as that which would be due to a diminution in the electric charge on P; it diminishes the effect of the sign we are considering, the further it is away the less will be this diminution and therefore the greater the negative effect.

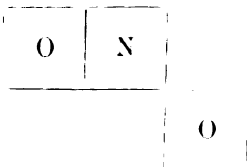
We shall consider some examples of this type of substituent. Let us take first  $\text{NO}_2$ , which has 17 electrons, sufficient to make two complete octets and leave one electron over, as in fig. 5. This radicle, represented by  $\text{O}=\text{N}=\text{O}$ ,



Fig. 5.



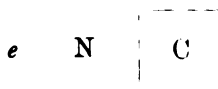
is a system of the type we are considering, with a positive  $\text{NO}_2$  and a detached electron; the radicle in this form would be attached to the rest of the molecule by the nitrogen atom. If it were attached by the oxygen atom the constitution of the radicle would be represented by



where there is no detached electron but an incompleted octet round the atom of oxygen which is to be bound to the parent molecule. As this form contains an incomplete octet it will as a substituent produce the same type of electrical effect as  $\text{OH}$ , or  $\text{Cl}$ . This is the type of  $\text{NO}_2$  which occurs in methyl nitrite, the other type is that found in nitromethane. The two types give electrical moments of opposite signs.

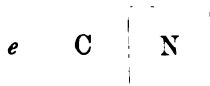
The most favourable arrangement of electrons for the production of electric effects of the second type, where the effect of substitution is of the same sign as that due to an increase in the negative charge on P, is evidently one where there is one electron over after saturating all the atoms.  $\text{NO}_2$  is a case of this kind,  $\text{CO OH}$  is another; here we have 17 electrons sufficient to give two complete octets and one over;  $\text{CN}$  has 9 electrons, these may be arranged in an octet surrounding the positive cores of both the carbon and nitrogen atoms, with an electron over. There are other arrangements of the electrons in the  $\text{CN}$  radicle which are not so favourable for the production of the second type of electrical effect. Thus the octet might only surround the nitrogen

Fig. 6.



atom as in fig. 6; with this arrangement the connexion would be made through the carbon atom. If the octet surrounded the carbon atom as in fig. 7, the connexion between

Fig. 7.



the radicle and the molecule with which it combines would be made through the nitrogen atom as in the isocyanides. In  $\text{H}-\text{C}=\text{O}$  we have eleven electrons, eight of these may be used to form an octet round the oxygen, two to bind the hydrogen to the carbon, and one remains detached; so that we should expect this radicle to produce an effect of the second type.

Thus we have seen that the electrical effect of replacing an atom of hydrogen by another atom or radicle may be represented by the introduction of an electric doublet at the hydrogen atom. The sign of the doublet will depend upon the nature of the radicle.

- A. The *positive* end of the doublet will be toward the molecule with which the hydrogen is combined and the negative end away from it if the radicle is of Type I., which includes  $\text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$ ,  $\text{OH}$ ,  $\text{NH}_2$ ,  $\text{CH}_3$ .

All these radicles and atoms contain 7 electrons, which can thus form a system which wants but one electron to form a complete octet.

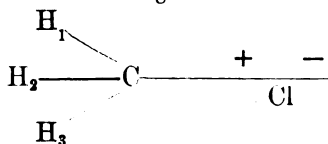
B. The *negative* end of the doublet will be toward the molecule with which the hydrogen is combined and the positive away from it if the radicle is of Type II., which includes  $\text{O}=\text{N}=\text{O}$ ,  $\text{OH}-\text{C}=\text{O}$ ,  $\text{H}-\text{C}=\text{O}$ ,  $\text{CN}$ .

In this type of radicle there is one electron over after providing for complete octets, thus there are 17 electrons in  $\text{NO}_2$  and  $\text{COOH}$  which leaves one electron over after two octets have been completed.

Miss Hoffert, in a very interesting paper in the 'Journal of the Society of Chemical Industry,' has called attention to the fact that those radicles and atoms which when introduced into the benzene ring cause a second substitution to take place in the ortho or para positions, contain one electron less than is required to form complete octets, while those which give rise to substitution in the meta position contain one electron more than is required for complete octets.

We shall now try to interpret in terms of chemical properties the change of the electrical field due to substitution. To take an example, suppose one of the hydrogen atoms in  $\text{CH}_4$  is replaced by an atom or radicle of Type I., say by chlorine. The difference in the electric fields of  $\text{CH}_4$  and

Fig. 8.



$\text{CH}_3\text{Cl}$  can be represented by an electric doublet at Cl whose positive end is toward C the centre of the carbon atom, and the negative end towards Cl (fig. 8). This doublet will produce an electric field which at  $\text{H}_1$ ,  $\text{H}_2$ ,  $\text{H}_3$ , the positions of the three hydrogen atoms, tends to drive away positive electricity and to attract negative. If the molecule  $\text{CH}_3\text{Cl}$  were in an ionized medium, this field would make the negative ions congregate more intensely round  $\text{H}_1$ ,  $\text{H}_2$ ,  $\text{H}_3$ , than they would have done if the fourth hydrogen atom had not been replaced by chlorine. Thus the field will concentrate the negative ions round the remaining hydrogen atoms and also repel

these atoms, and both effects will facilitate their replacement by other negative ions. Thus we see that where one carbon atom in a carbon compound has already been chlorinated it is more likely to be attacked still further by chlorine than a carbon atom none of whose hydrogen atoms have been replaced by chlorine. There are many illustrations of this effect. For example, when  $\text{H}_3\text{C}-\text{CH}_2\text{Br}$  is brominated still further a considerable excess of  $\text{H}_3\text{C}-\text{CHBr}_2$  over  $\text{BrH}_2\text{C}-\text{CH}_2\text{Br}$  is produced; *i. e.*, the carbon atom which has already been brominated is brominated again in preference to the one not already attacked.

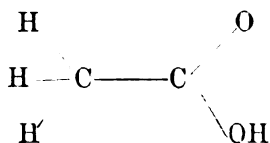
Again, it is a general rule in Organic Chemistry that "where an organic compound is submitted to oxidation the molecule is attacked at the part which already contains oxygen, that is, where oxidation has already begun" (Holleman's 'Organic Chemistry'). Since OH and O belong to type I. we see that the explanation we gave for the effect of chlorination applies also to this law.

Another illustration is that of vinyl chloride  $\text{H}_3\text{C}-\text{CH}_2\text{Cl}$ , this when exposed to chlorine in the light gives  $\text{H}_3\text{C}-\text{CHCl}_2$ .

Again,  $\text{CH}_3$  is a radicle of type I. *i. e.*, its substitution for hydrogen produces an electric field which tends to attract negative ions; thus in propylene  $\text{H}_3\text{C}.\text{CH}:\text{CH}_2$ , which we may regard as derived from ethylene by substituting  $\text{CH}_3$  for one of the hydrogens attached to  $\text{C}_1$ , the  $\text{CH}_3$  will make the central carbon more likely to attract halogen ions than  $\text{C}_2$  where no substitution has taken place, consequently, when propylene is acted upon by hydriodic acid the main product is  $\text{H}_3\text{C}.\text{CHI}.\text{CH}_3$ . In  $\text{H}_3\text{C}.\text{CBr}:\text{CH}_2$ , the central carbon is exposed to the effect of Br as well as  $\text{CH}_3$ , both belonging to type I., hence we should expect, as is the case, that when this compound is acted on by hydrogen bromide  $\text{H}_3\text{C}.\text{CBr}_2.\text{CH}_3$  is produced. In the compound  $\text{H}_3\text{C}.\text{CH}:\text{CHBr}$ , the end carbon is under the influence of Br while the central one is under that of  $\text{CH}_3$ , thus when hydrogen bromide is added, both  $\text{H}_3\text{C}.\text{CBrHCH}_2\text{Br}$  and  $\text{H}_3\text{C}.\text{CH}_2\text{CHBr}_2$  are formed.

Since the atoms and radicles of type I., produce, when they replace hydrogen, an electric field which tends to drive off the positive hydrogen atoms and thus produce free hydrogen ions, the entrance of these into a compound ought to increase its acidity. This is well marked in many cases, thus the replacement of two of the hydrogens in methyl alcohol by an atom of oxygen corresponding to the change to formic acid changes a weak base to a strong acid, presumably by facilitating the detachment of the hydrogen ion from the hydroxyl radicle. Again, while KOH is a strong base ClOH is an acid;

monochlor, dichlor and trichlor acetic acid are much stronger acids than acetic acid itself. The difference in strengths is so great that I do not think the whole of it can be ascribed to the direct effect of the kind we are considering, indeed the fact that acetic acid is a weaker acid than formic shows that other factors must be taken into consideration. Such a factor might be one of the following kind :—Acetic acid can decompose into  $\text{CH}_4$  and  $\text{CO}_2$  with complete separation of these constituents: if this is so, we might expect that at ordinary temperatures, when this separation is not effected, we might have in some of the molecules of acetic acid a grouping of the atoms and electrons corresponding to that of a molecular compound of  $\text{CH}_4$  and  $\text{CO}_2$ ; this need not be permanent but merely a phase passing back into the grouping represented by the usual formula for acetic acid, *i. e.*,



if we call this grouping phase II., the grouping corresponding to  $(\text{CH}_4\text{CO}_2)$  phase I., then the compound when in phase II. would be an acid, but would not be so when in phase I. Thus its strength as an acid would depend upon the proportion between the times it was in phases I. and II. respectively, or what is the same thing, on the proportion between the number of molecules which at any instant are in phases I. and II. If this view is correct then the strength of an acid cannot be calculated merely from the formula which represents its configuration when in its most acidic condition. We have to know whether the molecule spends the whole of its time in this condition, and if not, what are the duration and character of the other phases through which it passes. It may be that the introduction of chlorine into acetic acid may increase the duration of the more acidic condition as well as make that condition more intense than the corresponding one for acetic acid.

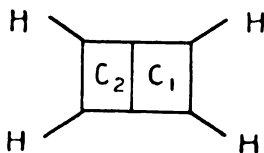
### *The Polarization of the Double Bond.*

When two carbon atoms are connected as in ethylene by a double bond, the electrons are distributed in two octets round the carbon atoms, the octets having four electrons in common. As the potential energy will clearly be a minimum



when the distribution of electrons is symmetrical about the plane bisecting the line  $C_1 C_2$  at right angles (fig. 9), this will be the stable distribution and there will not be any difference between the properties of the two carbon atoms. Suppose now, that one of the hydrogen atoms attached to  $C_1$  is replaced by an atom of chlorine. The effect of this, as we have seen, is to introduce at this atom an electric doublet whose positive end is towards  $C_1$ . The electrons between  $C_1$  and  $C_2$  in the octets will thereby be drawn closer to  $C_1$  and away from  $C_2$ , the density of the electrons on the  $C_1$  side of the double bond will be greater than that of those on the  $C_2$  side; the double bond will be polarized and the properties of the  $C_2$  will differ from those of the  $C_1$  carbon. If the displacements of the electrons were considerable the result would be that though the octet round  $C_1$  would remain complete it could no longer be regarded as sharing four electrons with the system round  $C_2$ ; thus  $C_2$  would no longer be surrounded by

Fig. 9.



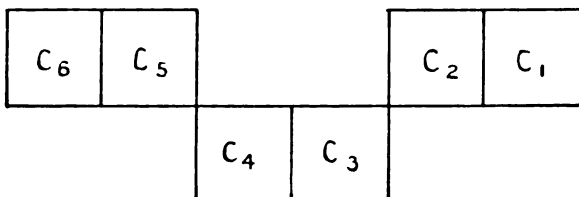
a complete octet, it would be unsaturated and could take up another electron and thus enter into combination with another atom, and the double bond would be converted into a single one. Thus on this view, *ceteris paribus*, addition compounds would be formed more freely with a compound like  $H_2CCHCl$ , than with one like  $H_2CCH_2$ .

But even when the displacement of the electrons is not sufficient to loosen the double bond, the movement of electrons from  $C_2$  towards  $C_1$  will diminish the attraction which these electrons exert on the positive part of an atom of hydrogen attached to  $C_2$  so that this hydrogen atom will be more easily detached than before the introduction of the chlorine. Again, the movement of the electrons away from  $C_2$  will tend to increase the chance of molecular compounds being formed in its neighbourhood. In the undisturbed position of the electrons  $C_2$  was coordinately saturated, it could not form either atomic or molecular compounds; with the movement of the electrons away from  $C_2$  this saturation will be relaxed,

and the possibility of a molecule forming part of the system round  $C_2$  increased. As the preliminary formation of "molecular compounds" is very often essential to chemical change, this effect will also increase the activity of  $C_2$ .

If instead of two carbon atoms we have a series arranged as in fig. 10, then the movement of the electrons from  $C_2$  towards  $C_1$  will diminish the repulsion which these electrons exerted on those in  $C_3$ , electrons will thus tend to crowd into  $C_3$  from  $C_4$ , thus the density of the electrons round  $C_3$  will be increased while the density of those round  $C_4$  will be diminished. Thus in a chain of carbon atoms of this kind the effect of the substitution of chlorine for hydrogen at one of them is to make the density of the electrons round successive carbon atoms alternately greater or less than the normal, *i.e.*, to make chemically inert and chemically active carbon atoms alternate with each other.

Fig. 10.



If instead of chlorine the substituent at  $C_1$  had been one of type II. giving rise to an electrostatic moment with the *negative* end towards  $C_1$ , the electrons would be displaced from  $C_1$  towards  $C_2$ ; this would increase the density of the electrons round  $C_2$  and decrease its chemical activity, the electrons moving towards  $C_2$  would exert an increased repulsion on those in  $C_3$ , reducing the density round  $C_3$  and thereby increasing the chemical activity of that atom.

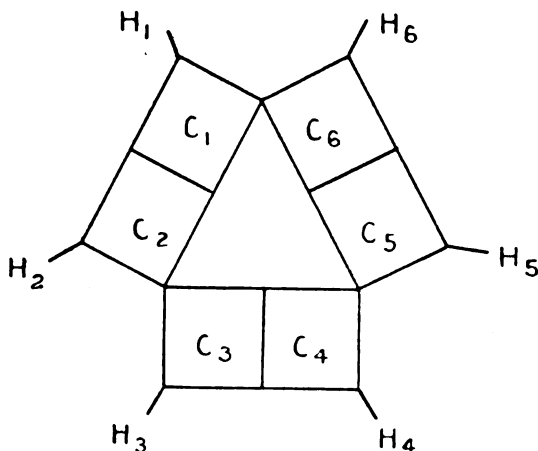
Thus when the substituent is of type I. the active carbons are those which are 1, 3, 5, .... places from the atom where the substitution took place; when the substituent belongs to type II. the active atoms are 2, 4, 6, .... places away from the substituent.

Polarization of the double bond could be produced without substitution by the presence of polar molecules or charged ions.

*On Benzene Substitutions.*

An interesting example of this principle is that of benzene substitutions. Thus let fig. 11 represent the arrangement of the atoms in the benzene ring, and suppose  $H_1$  the hydrogen attached to the carbon atom  $C_1$  is replaced by an atom or radicle of type I. From what we have just seen the carbon atoms in the ortho and para positions will become active since these are respectively 1 and 3 places from the carbon where substitution took place; those in the meta position will be inert. If, however, the hydrogen at  $C_1$  is replaced by an

Fig. 11.



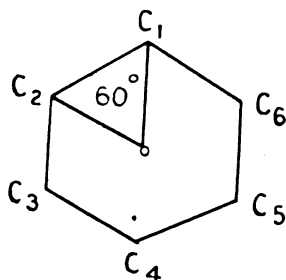
atom or radicle of type II., the carbons in the meta positions will be the active ones while those in the ortho and para positions will be inert. Now (see Holleman's 'Organic Chemistry,' English translation, p. 514) the substituents which direct a second substituent into the ortho and para positions are  $Cl$ ,  $Br$ ,  $I$ ,  $OH$ ,  $NH_2$ ,  $CH_3$ , while those which direct a second substituent into the meta positions are  $NO_2$ ,  $CO.OH$ ,  $CN$ ,  $HSO_3$ . It will be seen that this division is exactly the same as that arrived at from the consideration of the sign of the electric doublet which produces the same effect as the substitution of the atom or radicle for hydrogen.

*The Polarity of the Substituted Benzenes.*

Benzene itself is a non-polar substance and has a specific inductive capacity equal to the square of its refractive index,

the introduction of a substituent on our view introduces an electrical moment, *i.e.*, it makes the molecule polar, and should therefore endow the molecule with a high inductive capacity. The difference between the specific inductive capacities of the substituted benzene and benzene itself, estimated per molecule, is a measure of the moment of the doublet representing the effect of substitution. The substituted benzenes show, as a rule, very high specific inductive capacities, thus benzonitril has a specific inductive capacity of 26, nitrobenzol 33·4–37·4, benzol cyanide 16·7 (Walden, *Zeitschrift f. Phys. Chem.* lv. p. 232). There do not seem to be any measurements of the specific inductive capacity of bisubstituted benzenes; these would be of considerable interest. Let us consider first the case when both substituents are of the same kind and that  $I$  is the moment of the doublet for one substitution. Now

Fig. 12.



suppose that a second substitution takes place, the electrostatic moment of the molecule will depend upon whether the second substituent goes into the para, ortho, or meta position.

Neglecting the deflexion of the two doublets due to their action on each other we see from fig. 12 that :

1. If the second constituent goes into the para position the resultant moment is zero.
2. If it goes into the ortho position the resultant moment is

$$\{I^2 + I^2 + 2I^2 \cos 60^\circ\}^{1/2} = \sqrt{3}I.$$

3. If it goes into the meta position the resultant moment is

$$\{I^2 + I^2 + 2I^2 \cos 120^\circ\}^{1/2} = I.$$

Thus a para substitution destroys the moment and should therefore make the molecule non-polar and the dielectric capacity normal.

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A meta substitution leaves the moment unchanged in magnitude.

An ortho substitution increases the moment and therefore increases the specific inductive capacity.

It would seem that determinations of the specific inductive capacity might be useful in determining whether the second substituent went into the para, ortho, or meta position.

If the second substituent is not the same as the first, thus if  $I'$  is the moment due to the second, the moment of the molecule if the second substituent goes into :

- (1) The para position is  $I - I'$ .
- (2) The ortho position is  $(I^2 + I'^2 + II')^{1/2}$ .
- (3) The meta position is  $(I^2 + I'^2 - II')^{1/2}$ .

If  $I$  and  $I'$  have the same sign, *i. e.*, if both substituents belong to the same type, the specific inductive capacity will be least for the para position and greatest for the ortho—that for the meta position will be between the values for the para and ortho.

If, however, the two substituents belong to different types  $I'$  will be of the opposite sign to  $I$ , and the specific inductive capacity will be *greatest* in the para position and least in the ortho.

LV. *On a Second Approximation to the Quantum Theory of the Simple Zeeman Effect and the Appearance of New Components.* By A. M. MOSHARRAFA, *King's College, London* \*.

§ 1. *The Hypothetical Path of Equal Energy.*

IN a previous paper † a first approximation to the theory of the simple Zeeman effect was put forward, based on the extended form of the quantum restrictions, viz.

$$\int_0 (p_i - ea_i) dq_i = n_i h, \quad i = 1, 2, 3, \dots, \quad \dots \quad (1)$$

where  $a$  is the magnetic vector potential and the integration extends from  $q_i = \text{minimum}$  to  $q_i = \text{maximum}$  and back again. It was found that the method of separation of the variables could be successfully applied in the presence of the field  $H$ , provided all terms of higher order than the first in  $H$  were

\* Communicated by Prof. O. W. Richardson, F.R.S.

† Roy. Soc. Proc. A. vol. cii. p. 529 (1923). This will be referred to freely.

neglected. In this paper we shall show that the method can still be applied, without any restriction as to the degree of approximation, to a hypothetical motion which possesses the same energy as the actual motion.

Let  $\Sigma^*$  be one of the actual paths of the electron in the presence of the field. Thus  $\Sigma$  is completely defined by the following six equations in spherical polar coordinates† with the origin in the nucleus and Oz in the direction of H :

$$\left. \begin{aligned} d(m\dot{r})/dt - mr\dot{\theta}^2 - mr\sin^2\theta\dot{\psi}^2 &= -eE/r + K_r, \quad (\alpha) \\ \frac{1}{r} d(mr^2\dot{\theta})/dt - mr\sin\theta\cos\theta\dot{\psi}^2 &= K_\theta, \quad (\beta) \\ \frac{1}{r\sin\theta} d(mr^2\sin^2\theta\dot{\psi})/dt &= K_\psi, \quad (\gamma) \end{aligned} \right\} \quad (2)$$

$$\left. \begin{aligned} \int_0 p_r dr &= n_1 h, \quad (\alpha) \\ \int_0 p_\theta d\theta &= n_2 h, \quad (\beta) \\ \int_0 (p_\psi - m_0 \omega r^2 \sin^2\theta) d\psi &= n_3 h, \quad (\gamma) \end{aligned} \right\} \quad (3)$$

where  $m$  is the mass of the electron [variable],  $m_0$  is the value of  $m$  for zero velocity,  $(-e)$  and  $E$  are the charges on the electron and nucleus respectively,  $\omega$  is given by

$$\omega = eH/2m_0c, \quad (4)$$

and  $K$  is the so-called "Coriolis" force acting on the electron on account of its motion in the magnetic field, being equal per unit charge to the vector product of the velocity and the field. Thus

$$\left. \begin{aligned} K_r &= -eHr\sin^2\theta\dot{\psi}/c, \quad (\alpha) \\ K_\theta &= -eHr\sin\theta\cos\theta\dot{\psi}/c, \quad (\beta) \\ K_\psi &= eH(\dot{r}\sin\theta + r\cos\theta\dot{\theta})/c. \quad (\gamma) \end{aligned} \right\} \quad (5)$$

Consider a hypothetical path  $\Gamma$  defined by the six equations obtained from (2) and (3) by putting  $K_r = K_\theta = K_\psi = 0$  in the former but without altering the latter in any way.  $\Sigma$  can thus be conceived to be derived from  $\Gamma$  by the operation of

\*  $\Sigma$  and  $\Gamma$  here used to denote the complete specific motions in the two respective cases.

† The proof is equally valid for any set of coordinates. We choose spherical polars in this section merely because they are adopted in the rest of the paper.

the coriolic forces alone \*. Now the element of work done by the coriolic forces is equal to

$$(K_r v_r + K_\theta v_\theta + K_\psi v_\psi) dt,$$

where  $v$  is the velocity of the electron at the time considered. And, on using the values of  $v_r$ ,  $v_\theta$ , and  $v_\psi$  in terms of the coordinates, viz.

$$v_r = \dot{r}, \quad v_\theta = r\dot{\theta}, \quad v_\psi = r \sin \theta \dot{\psi},$$

this is seen from (5) to be identically equal to 0. In other words, the introduction of the coriolic forces alone cannot affect the energy of the electron, and therefore

$$W(\Sigma) = W(\Gamma) = W, \text{ say, } \dots \dots (6)$$

where  $W(\Sigma)$  and  $W(\Gamma)$  are the respective energies of the two paths. Hence we may calculate the value of  $W$  by considering the motion in  $\Gamma$  instead of in  $\Sigma$ .

## § 2. The Expression for $W$ .

Any path  $\Gamma$  is a "relativity ellipse," the dimensions of which are defined by the modified quantum restrictions (3). We thus have for  $\Gamma$ , from the analysis given in § 2 of our previous paper, on putting  $H=0$ :

$$\left. \begin{aligned} p_r &= m\dot{r} = \sqrt{[A + 2B/r + C/r^2]}, & (\alpha) \\ p_\theta &= mr^2\dot{\theta} = \sqrt{[p^2 - F^2/\sin^2 \theta]}, & (\beta) \\ p_\psi &= mr^2 \sin^2 \theta \dot{\psi} = F, & (\gamma) \end{aligned} \right\} \quad (7)$$

where  $A$ ,  $B$ , and  $C$  are given by

$$\left. \begin{aligned} A &= 2m_0 W (1 + W/2m_0 c^2), & (\alpha) \\ B &= e F m_0 (1 + W/m_0 c^2), & (\beta) \\ C &= -(p^2 - e^2 E^2/c^2), & (\gamma) \end{aligned} \right\} \quad (8)$$

and  $p$  and  $F$  are constants. From (3) and (7) we have

$$\left. \begin{aligned} \int_0^1 \sqrt{[A + 2B/r + C/r^2]} dr &= n_1 h, & (\alpha) \\ \int_0^1 \sqrt{[p^2 - F^2/\sin^2 \theta]} d\theta &= n_2 h, & (\beta) \\ \int_0^{2\pi} [F - m_0 \omega r^2 \sin^2 \theta] d\psi &= n_3 h, & (\gamma) \end{aligned} \right\} \quad (9)$$

\* It must be clearly understood that this cannot be achieved by actually introducing the magnetic field, since the introduction of a magnetic field involves other forces besides  $K$ , viz. the induction forces, which do in fact alter the energy.

and the first two integrals yield as before

$$\left. \begin{aligned} 2\pi i[\sqrt{C+B/\sqrt{A}}] &= n_1 h, \quad \dots \quad (\alpha) \\ 2\pi(p-F) &= n_2 h, \quad \dots \quad (\beta) \end{aligned} \right\} \quad (10)$$

To evaluate the third integral we have to deal with

$$I = \omega m_0 \int_0^{2\pi} r^2 \sin^2 \theta d\psi, \quad \dots \quad (11)$$

or since

$$m = m_0/\sqrt{(1-\beta^2)}, \quad \dots \quad (12)$$

we have from (7 γ), (11), and (12),

$$I = \omega F \int_0^T \sqrt{(1-\beta^2)} dt, \quad \dots \quad (13)$$

where T is the time from  $\psi=0$  to  $\psi=2\pi$ . Let

$$T = T_0 + \delta_\omega T + \delta_\alpha T + \dots, \quad \dots \quad (14)$$

where  $\delta_\omega T$  and  $\delta_\alpha T$  are first-order terms in  $\omega$  and  $\alpha$  respectively,  $\alpha$  being given by

$$\alpha = (2\pi)^2 e^2 E^2 / h^2 c^2, \quad \dots \quad (15)$$

and  $T_0$  being the value of T calculated for  $\omega=\alpha=0$ .

We have as a first approximation to the value of I:

$$I = \omega F T_0 + \dots, \quad \dots \quad (16)$$

where

$$T_0 = (n_1 + n)^3 / 2N, \quad \dots \quad (17)$$

N being the Rydberg constant

$$N = (2\pi)^2 m_0 e^2 E^2 / 2h^3 \quad \dots \quad (18)$$

and

$$n = n_2 + n_3. \quad \dots \quad (19)$$

From (9 γ), (11), and (16), we have

$$2\pi F = n_3 h [1 + \omega T_0 / 2\pi + \dots]. \quad \dots \quad (10 \gamma)$$

Thus, as a first approximation, the motion in  $\Gamma$  is defined by exactly the same equations as in the ordinary Bohr-Sommerfeld atom, except that  $n_3$  is now replaced by

$$n_3(1 + \omega T_0 / 2\pi).$$

Hence, using (17),

$$T_0 + \delta_\omega T = [n_1 + n_2 + n_3(1 + \omega T_0 / 2\pi)]^3 / 2N$$

to the first order,

so that

$$\delta_\omega T / T_0 = 3n_3 \omega T_0 / 2\pi(n + n_1). \quad \dots \quad (20)$$



Now I can be put in the form

$$I = \omega F(1 + \delta_\omega T/T_0) \int_0^{T_0 + \delta_\alpha T} \sqrt{1 - \beta^2} dt \quad (21)$$

to the second order, where the last integral is evaluated for  $\omega = 0$ . This evaluation is quite independent of a magnetic field, and merely relates to the Bohr-Sommerfeld atom. Quoting here the result given in the Appendix (*q. v.*) for this integral, and using the value for  $F$  given by (10  $\gamma$ ), we have

$$I = n_3 h \{ 1 + f_1(n) \cdot \omega T_0 / 2\pi - \alpha f_2(n) \} \omega T_0 / 2\pi, \quad (22)$$

where

$$\left. \begin{aligned} f_1(n) &= 1 + 3n_3 / (n + n_1), & (\alpha) \\ f_2(n) &= [1 + 5n_1 / 2n + n_1^2 / 2n^2] / (n_1 + n)^2, & (\beta) \end{aligned} \right\} \quad (23)$$

Equations (9  $\gamma$ ), (11), and (22) finally yield

$$2\pi F = n_3 h \{ 1 + \omega T_0 / 2\pi + f_1(n) (\omega T_0 / 2\pi)^2 - f_2(n) \cdot \alpha \omega T_0 / 2\pi + \dots \}. \quad (10 \gamma a)$$

Thus the equations defining  $\Gamma$  are identical, to the second order of small quantities, with those defining the normal atom if we write  $n_3'$  for  $n_3$ , where

$$n_3' = n_3 \{ 1 + \omega T_0 / 2\pi + f_1(n) \cdot (\omega T_0 / 2\pi)^2 - f_2(n) \cdot \alpha \omega T_0 / 2\pi \}. \quad (24)$$

The change in energy can thus at once be calculated from the normal expression for the energy by making this substitution. The normal expression for the energy can be put in the form

$$W_{\text{norm.}} = -Nh \{ 1 + \alpha \phi_1(n_1/n) / (n_1 + n)^2 + \alpha^2 \phi_2(n_1/n) / (n_1 + n)^4 + \dots \} / (n_1 + n)^2, \quad (25)$$

where

$$\left. \begin{aligned} \phi_1(n_1/n) &= 1/4 + n_1/n, & (\alpha) \\ \phi_2(n_1/n) &= 1/8 + 3n_1/4n + 3n_1^2/2n^2 + n_1^3/4n^3; & (\beta) \end{aligned} \right\} \quad (26)$$

from which we calculate, using (23), (26  $\alpha$ ), and (17) :

$$\left. \begin{aligned} \delta_\omega W &= n_3 h \omega / 2\pi, & (\alpha) \\ \delta_\alpha W &= -Nh \alpha \phi_1(n_1/n) / (n_1 + n)^4, & (\beta) \\ \delta_{\omega^2} W &= (n_1 + n)^3 n_3 h \omega^2 [1 + 3n_3 / 2(n_1 + n)] / 2 \cdot (2\pi)^2 N, & (\gamma) \\ \delta_{\alpha^2} W &= -Nh \alpha^2 \phi_2(n_1/n) / (n_1 + n)^6, & (\delta) \\ \delta_{\omega, \alpha} W &= -n_3 \omega \alpha h / 4\pi (n + n_1)^2, & (\epsilon) \end{aligned} \right\} \quad (27)$$

§ 3. *Significance of the Results of § 2, and General Character of the Zeeman Decomposition.*

Of the five increments of energy given by (27) the first two merely give the simple Zeeman triplet and the first-order fine structure respectively, as already dealt with in the last paper. (27  $\delta$ ) is the second-order term for the fine structure and leads to a change in wave-length of the order  $10^{-5}$  Å, which is much too small to be detected. With regard to the other two terms, we have from (27)

$$\delta_{\omega, \alpha} W / \delta_{\omega^2} W = -2\pi\alpha N / \omega f_1(n)(n+n_1)^5, \quad \dots \quad (28)$$

and on substituting the values for  $\omega$ ,  $\alpha$ , and  $N$  for hydrogen ( $E=e$ ), viz.

$$\omega / 2\pi = 1.406 \times 10^6 \text{ H}, \quad \dots \quad (29)$$

$$\alpha = 5.5 \times 10^{-5}, \quad \dots \quad (30)$$

$$N = 3.290 \times 10^{15}, \quad \dots \quad (31)$$

we have, since  $f_1(n) (=) 1$ ,

$$\delta_{\omega, \alpha} W / \delta_{\omega^2} W (=) 10^5 / \text{H}(n_1+n)^5, \quad \dots \quad (32)$$

where  $(=)$  stands for equality of order of magnitude only.

Now the smallest value for  $H$  which will give a measurable second-order effect is of the order  $10^6$  Gauss; so that we have for a measurable effect:

$$|\delta_{\omega, \alpha} W / \delta_{\omega^2} W| < 1/10(n_1+n)^5.$$

Thus for the Balmer Series ( $n_1+n=2$ ) the ratio is less than  $10^{-2}$ , and it is still less for the enhanced series ( $n_1+n>2$ ). It must, nevertheless, be noted that for fields higher than  $H(=)10^8$  Gauss, although the above ratio is reduced to less than  $10^{-4}$ , yet the  $\delta_{\omega, \alpha} W$  term would lead to measurable effects. Such very high fields are, however, not likely to be attained at present. We thus see that the only second-order term that has any importance in (27) is the term in  $\omega^3$ , and the effect of the field may therefore still be described as a splitting of each of the fine structural components into a Zeeman multiplet. This multiplet is no longer a simple triplet, however, but may be described as a splitting of each of the components of the simple Zeeman triplet into a number of "sub-components." The number of these sub-components depends on  $(n_1+n)$ , i. e. on the value of the constant series term of the spectral "line" in question. Thus there are  $(n+n_1+1)$  sub-components of the middle member of the triplet ( $m_3-n_3=0$ ),  $(n+n_1+1)$  of the "violet" member ( $m_3-n_3=+1$ ), and

$(n+n_1)$  of the "red" member ( $m_3-n_3=-1$ ), altogether  $3(n+n_1)+2$  sub-components. One of these, belonging to the middle member of the triplet and corresponding to  $m_3=n_3=0$ , always occupies the position of the original line. It is also to be noted that, as in the case of the Stark effect\*, this second-order deviation from symmetry increases as we approach the more violet end of a given series, *i. e.* as  $m_1+m$  increases. This is on account of the occurrence of  $(m_1+m)^3$  in the expression for  $\delta\nu$  [see equations (33) and (34) below]. Thus for the Balmer Series the effect would be more pronounced for  $H_\beta$  than for  $H_\alpha$ , and so on.

#### § 4. Application to the Balmer Series.

We choose  $H_\gamma$  as an example. We have from (27), on restricting ourselves to the second-order effect and dropping the suffix  $\omega^2$  for brevity,

$$\delta\nu = \omega^2(Z_m - Z_n)/2N \cdot (2\pi)^2, \quad \dots \quad (33)$$

where

$$\left. \begin{aligned} Z_m &= (m_1+m)^3 m_3 [1 + 3m_3/2(m_1+m)], \\ Z_n &= (n_1+n)^3 n_3 [1 + 3n_3/2(n_1+n)]. \end{aligned} \right\} \quad \dots \quad (34)$$

For  $H_\gamma$ , since  $m_1+m=5$ ,  $n_1+n=2$ , (34) reduces to

$$\left. \begin{aligned} Z_m &= 125m_3(1 + 3m_3/10), \\ Z_n &= 8n_3(1 + 3n_3/4). \end{aligned} \right\} \quad \dots \quad (34a)$$

And from (33) we have for the increment of wave-length  $\delta\lambda$

$$\delta\lambda = -\lambda^2 \omega^2 [Z_m - Z_n]/2Nc \cdot (2\pi)^2. \quad \dots \quad (35)$$

On putting  $\lambda = 434 \times 10^{-4}$  and substituting for  $N$  and  $\omega$  from (31) and (29) respectively for a hypothetical magnetic field:

$$H = 10^6 \text{ Gauss}, \quad \dots \quad (36)$$

we have

$$\delta\lambda' = -1.89 \times 10^{-3} [Z_m - Z_n], \quad \dots \quad (37)$$

where  $\delta\lambda' = \delta\lambda \times 10^8$ , *i. e.* where  $\delta\lambda'$  is measured in Angström units.

The different possible values of  $Z_m$  and  $Z_n$  are given in Table A, and the values of  $(Z_m - Z_n)$  corresponding to the three components of the simple Zeeman triplet are given in Table B, together with the values of  $\delta\lambda'$  calculated from (37). Table B has been arranged so that the respective positions

\* See A. M. Mosharrafa, Phil. Mag. vol. xlix. p. 373 (August 1922).

TABLE A.

	a.	b.	c.	d.	e.	f.		I.	II.	III.
$m_s =$	5	4	3	2	1	0	$n_s =$	2	1	0
$Z_m =$	1562.5	1100	712.5	400	162.5	0	$Z_n =$	40	14	0

TABLE B.

	"Violet" Component, $m_s - n_s = +1.$			Middle Component, $m_s - n_s = 0.$			"Red" Component, $m_s - n_s = -1.$	
	I. c.	II. d.	III. e.	I. d.	II. e.	III. f.	I. e.	II. f.
$Z_m - Z_n$ .....	672.5	386	162.5	360	148.5	0	122.5	-14
$\delta\lambda$ .....	-1.27	-.73	-.31	-.68	-.28	0	-.23	+0.3*

of the sub-components are, in each of the three cases, the same as they would appear on a photographic plate with the usual convention. We note that all displacements are towards the violet, except in the case of one of the sub-components of the red component, which is very slightly displaced towards the red. The greatest value of  $(-\delta\lambda')$  occurs for the violet component, and the least value for the red component: and this applies to all members of the Balmer series.

### Summary.

- (1) A second approximation to the theory of the simple Zeeman effect is worked out, based on the extended form of the quantum restrictions already adopted in a previous paper.
- (2) It is shown that the method of separation of the variables can be successfully applied for higher approximations than the first to a hypothetical motion which possesses the same energy as the actual motion.
- (3) The analysis takes account of the refinement of Relativity, but it is shown that the second-order effect of this refinement is negligible compared with that of the field.
- (4) The theory predicts a modification in the simple Zeeman triplet, which may be described as a splitting of each of its three components into a number of "sub-components." The general character of these sub-components is discussed.
- (5) The results are worked out fully in the case of  $H_\gamma$  for a hypothetical field of  $10^6$  Gauss, where second-order displacements ranging from  $+0.3$  Å. to  $-1.27$  Å. are predicted.

### APPENDIX (to § 2).

To find  $\int_0^{T_\psi} \sqrt{(1-\beta^2)} dt$  for the Bohr-Sommerfeld atom, where  $T_\psi$  is the time from  $\psi=0$  to  $\psi=2\pi$ :

Let  $(r, \phi)$  be polar coordinates in the plane of motion of the electron, so that

$$\tan \phi = \tan \psi \cos \alpha, \quad \dots \dots (i.)$$

where  $\alpha$  is the angle between the planes of  $\psi$  and  $\phi$ , and the initial lines  $\phi=0$ ,  $\psi=0$  are both perpendicular to the line of intersection of these two planes. We see from (i.) that as  $\psi$  changes from 0 to  $2\pi$ ,  $\phi$  changes

from 0 to  $2\pi$  also, so that we have

$$T_\psi = T_\phi, \quad \dots \dots \dots (ii.)$$

where  $T_\phi$  is the period for  $\phi$ . Let  $T_r$  be the time from  $r$ =minimum to  $r$ =maximum and back again. We have by a well-known result to the first order in  $1/c^2$ :

$$T_\phi = T_r(1 - e^2 E^2 / 2 p_0^2 c^2), \quad \dots \dots \dots (iii.)$$

or since

$$p_0 = nh/2\pi, \quad \dots \dots \dots (iv.)$$

we have from (ii.), (iii.), and (iv.)

$$T_\psi = T_r(1 - \alpha/2n^2), \quad \dots \dots \dots (v.)$$

where  $\alpha$  is defined by equation (15) of the text. Thus to the first order in  $\alpha$

$$\int_0^{T_\psi} \sqrt{1 - \beta^2} dt = (1 - \alpha/2n^2) \int_0^{T_r} \sqrt{1 - \beta^2} dt. \quad \dots (vi.)$$

Now we see from (7  $\alpha$ ) and (12) of the text that

$$\sqrt{1 - \beta^2} dt = m_0 dr / \sqrt{A + 2B/r + C/r^2};$$

so that

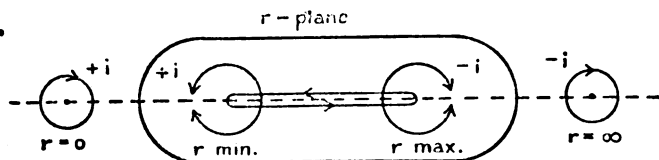
$$\int_0^{T_r} \sqrt{1 - \beta^2} dt = -m_0 J_r, \quad \dots \dots \dots (vii.)$$

where

$$J_r = \int_0^{T_r} dr / \sqrt{A + 2B/r + C/r^2} \quad \dots (viii.)$$

and the negative sign is introduced on account of the negative nature of the integrand.  $J_r$  may now be evaluated by the usual method of contour integration in the complex plane. We have to find the residues of the integrand at  $r=0$  and  $r=\infty$ . At  $r=0$  it behaves as

$$\frac{1}{\sqrt{C}} \int_0^r r dr (1 + Ar^2 + 2Br)^{-1/2},$$



which is regular. So that putting  $r=1/s$ , we have

$$\left. \begin{aligned} J_r &= -\frac{1}{\sqrt{A}} \int_0^1 (1 - Bs/A + \dots) ds/s^2 \\ &= -2\pi i \times B/A\sqrt{A}, \end{aligned} \right\} \quad \dots (ix.)$$

where it is observed that the sense of rotation at  $r=\infty$  is

negative. Also since  $(-1/\sqrt{A})$  is seen from (ix.) to govern the sign of the integrand at  $r=\infty$  it follows (see figure) that  $(-1/\sqrt{A})$  must be negative and imaginary, and therefore  $\sqrt{A}$  must be taken as the negative (imaginary) root of  $A$ . On substituting for  $A$  and  $B$  in (ix.) from (8) of the text we have

$$J_r = -2\pi i e E m_0 [2m_0 W]^{-3/2} [1 + W/4m_0 c^2 + \dots],$$

which yields to the first order on substituting for  $W$  from (25),

$$J_r = -(n_1 + n)^3 h^3 [1 - \alpha \{ \frac{1}{4} + 3\phi_1(n_1/n) \} / 2(n_1 + n)^2] / (2\pi e E m_0)^2, \quad \dots \quad (\text{x.})$$

and from (vi.), (vii.), and (x.) we have

$$\int_0^T \sqrt{(1-\beta^2)} dt = T_0 [1 - \alpha f_2(n)], \quad \dots \quad (\text{xi.})$$

where  $T_0$  has the same meaning as in the text and

$$\begin{aligned} f_2(n) &= \{ \frac{1}{4} + 3\phi_1(n_1/n) + (1 + n_1/n)^2 \} / 2(n_1 + n)^2 \\ &= [1 + 5n_1/2n + n_1^2/2n^2] / (n_1 + n)^2 \text{ from (26 } \alpha \text{).} \end{aligned}$$

This is the result quoted in the text.

January 1923.

LVI. *Electrical Discharges in Geissler Tubes with Hot Cathodes.* By W. H. MCCURDY, M.A., 1851 Exhibition Scholar, Princeton University\*.

IN a recent number of the 'Physical Review,' Duffendack† reported results obtained from work on low-voltage arcs, stimulated by the emission from a hot cathode, in diatomic gases. As his work dealt only with the arc characteristics, it was thought possible that additional light might be thrown on the process of ionization by a study of the discharge in Geissler tubes, if a hot filament were used as cathode to stimulate the discharge. This eliminated the uncertainty as to the source of the electrons which produced the ionization in the tube, and, at the same time, overcame the very high cathode fall of potential encountered in cold electrode tubes. With an apparatus provided with a hot cathode and a movable anode, it should be possible to study the successive stages in

\* Communicated by Professor K. T. Compton.

† Phys. Rev. vol. xx. No. 6, p. 665.

the type of discharge as the type changes from the characteristic arc type at short distances to the characteristic Geissler tube type at greater distances. This may aid in identifying the causes of various features of the Geissler tube discharge.

The work here recorded was divided into three parts, which will be treated separately :—

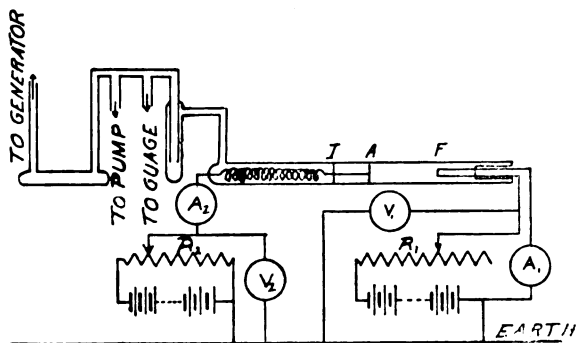
(1) Relation between current through the tube and potential applied to the tube; also observations on the appearance of the discharge under various conditions.

(2) Relations existing between the filament temperature pressure of the gas, and the least voltage ( $V_m$ ) necessary to maintain the discharge in hydrogen.

(3) Similar observations in mercury vapour.

The apparatus used is shown in fig. 1, as are also the electrical connexions.

Fig. 1.



The filament (F) was a tungsten spiral of only a few turns, which served to concentrate the heat at the centre, thus making it possible to obtain a reasonably high electron emission without a large potential drop across the filament. This potential fall was never more than 3.75 volts; thus, assuming that the discharge was maintained to the centre of the filament, which seemed probable as it was the part of greatest electron emission, the correction was never more than 1.8 volt. Further, as the voltage across the tube was applied between the negative terminal of the filament and the anode, the correction due to potential drop was approximately balanced by that due to the initial velocities of emission of electrons from the filament. Consequently the voltages given in the following data are the actual voltmeter ( $V_m$ ) readings. The anode (A) was either a nickel or an



aluminium disk with a piece of soft iron (I) attached to it, by means of which it was possible to place the anode at any desired position. The potential was supplied by a battery of accumulators and regulated by a rheostat ( $R_2$ ), the current being measured by the milli-microammeter ( $A_2$ ).

Two tubes of hard glass were used, one of diameter 4.0 cm. and the other 2.8 cm. Both were thoroughly baked out, and the filaments glowed until no appreciable amount of gas was given off.

The hydrogen used was obtained by the electrolysis of dilute sulphuric acid, dried and purified by phosphorus pentoxide and coconut charcoal in liquid air. The charcoal was so placed as to serve both as a purifying agent and as a reservoir to replace the hydrogen "cleaned up" by the discharge. The discharge was sustained before any readings were taken until the pressure, as measured on the McLeod gauge, no longer decreased.

PART I. — *Relation between current through the tube and potential applied to the tube; also observations on the appearance of the discharge under various conditions.*

The filament current was adjusted to the amount which gave the lowest value to the potential necessary to maintain the discharge at the distance between electrodes being used; then, with this current constant, the potential across the tube was gradually increased up to values of from 80 to 100 volts, and the current through the tube noted at suitable intervals. The potential was then decreased and current readings taken at intervals as when it was being increased. The whole process was then repeated at different distances and pressures.

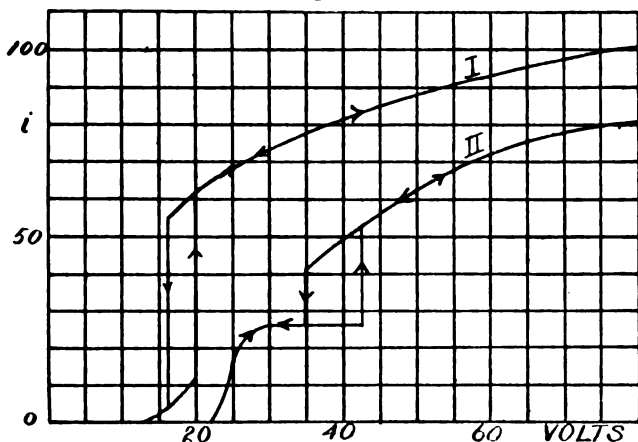
The relation between the current and voltage for two typical cases is shown in fig. 2. Curve I. shows the relation that was found to hold with the 4.0-cm. tube and at pressures about 0.4 mm. at distances less than about 1.2 cm. At lower pressures this sort of a relation would be found to hold at slightly greater distances. Under conditions given there was only one discontinuous change in the current, after which it gradually increased towards a maximum value. It will also be noted that the discharge was maintained at lower voltages than those necessary to start it, which has been explained by Duffendack\* as due to the fact that the potential distribution is more favourable for maintaining the discharge if there is a region of positive space charge surrounding the cathode. Curve II. represents the type of relation that existed

\* *Loc. cit.*

at distances greater than 1.2 cm. Here there were two distinctly marked discontinuities as the potential was increased, and sometimes, though not always, two as it was decreased. It will further be noticed from the figure that, for a portion of the region of voltage between the two discontinuities, the current remained constant as the voltage was increased. In some cases it was found to decrease with an increase in voltage. An explanation for this has not yet been found.

The two breaks in current at the greater distances were found to be associated with the appearance or disappearance

Fig. 2



of two distinct types of discharge, which were termed types A and B. This phenomenon was also found by MacLennan\* in his work on low-voltage arcs in cadmium. Type A showed very feeble luminosity, and the current associated with it was much smaller than that which was found with type B. The striations which, in the discharge in cold electrode tubes, form the positive column, extended well in toward the cathode. An increase in potential caused them to approach the cathode at a constant distance of separation, new striations appearing at the anode as the first ones disappeared at the cathode.

Type B showed strong luminosity, and the current was much larger. The appearance of the discharge was the same as that in the cold electrode tubes, with a well-defined dark space but rather diffuse negative glow. In this case the striations approached the anode at a constant distance of

\* Proc. Phys. Soc., Dec. 1918.

separation as the voltage increased, but no new striations appeared as the original ones disappeared at the anode.

The change in distribution of luminosity in the tube indicated that there must be a corresponding change in potential distribution between the electrodes. The two distributions possible which permit that the discharge may be maintained are a high cathode fall and the usual gradually increasing gradient in the region shortly in front of the negative dark space, or a cathode fall of only the ionizing potential of the gas at the cathode and a higher potential gradient in the dark space which may be shorter and a second region of ionization at the end of the dark space. The first distribution would cause intense ionization at the cathode, and thus a high space-charge is built up and the positive ions are drawn into the cathode at a relatively high velocity which would diminish the probability of recombination. Under such conditions it is possible that the proportion of the current carried by positive ions is comparable with the electron current; at any rate, the electron emission from the cathode must be increased by the building up of the high potential gradient at the cathode by the positive space charge. On the other hand, when the cathode fall is much smaller (about the ionizing potential of hydrogen) the ionization at the cathode is less, and consequently the positive space-charge is less. Also the positive ions produced in the second region (at the end of the dark space) have a very small chance of reaching the cathode before recombination, so contribute little or nothing to the current. Consequently, a smaller current is to be expected with such a distribution of potential.

The distance of separation of the striations was not affected by changes in either the filament current or the potential applied to the tube, which is in accordance with the equation for the distance between striations in cold electrode tubes

$d = \frac{2r^{1-m}}{p^m}$  \*, where  $d$  is the distance between the striations,  $r$  the radius of the tube, and  $p$  the pressure in the tube,  $m$  having a value of about .5.

The spectra observed in both types appeared to be the same, differing only in intensity. The region of the positive column showed a strong band spectrum and weak Balmer lines, while the region near the cathode showed strong Balmer lines and very little trace of the band spectrum.

\* Wehner, *Ann. der Physik*, xxxii. p. 49 (1910).

The position of the striations under different conditions was found to change as follows :—

Type B discharge :

(1) With filament current kept constant, they *approached* the anode as the potential applied to the tube was *increased*.

(2) With potential across the tube kept constant, they *approached* the anode as the filament current was *decreased*.

(3) With current through the tube kept constant, they *approached* the anode as the potential across the tube was *increased*.

Type A discharge :

With filament current kept constant, they *receded* from the anode as the potential across the tube was increased.

PART II.—*Relation between the pressure of the gas, the filament current, and the least voltage ( $V_m$ ) necessary to maintain the discharge in hydrogen.*

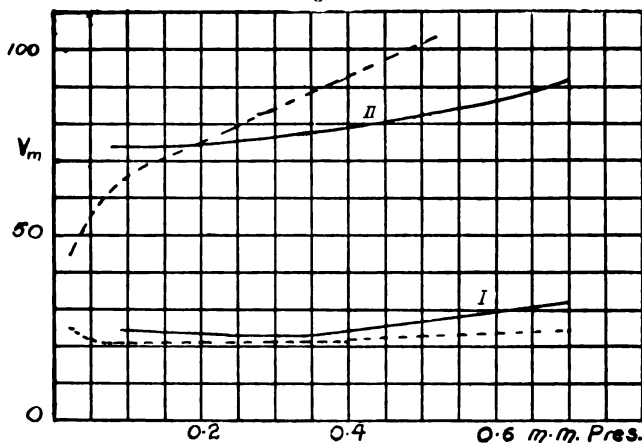
The apparatus used for this part of the investigation was the same as that shown for the first part.

The method employed was to determine the filament current at which the voltage necessary to maintain the discharge was a minimum, and to repeat this determination at various anode distances and gas pressures. This repetition was found necessary for the different distances and pressures on account of the variation of the behaviour of the maintaining voltage as the filament current was changed, when the anode was situated in the positive column. This was due to the high potential gradient in the vicinity of the striations, and, as was shown in the previous work, changes in the filament current cause a change in the position of the striations, hence a change in potential distribution.

The results of the work at various distances and pressures are indicated in the curves of fig. 3. Here Curve I. gives the variation of the least maintaining voltage  $V_m$  with pressure changes at an anode distance of 2.4 cm. in a tube 4.0 cm. diameter ; curve II., the same with a 10-cm. distance, with a tube 4.0 cm. in diameter. The continuous curves here represent the voltage at which type B discharge disappeared, while the dotted lines give the disappearing potentials found for type A. It will be observed that at the larger distances the pressure at which  $V_m$  for type A increased was not reached. It was found, however, that at lower pressures it was very difficult to start the discharge, and it disappeared at

voltages higher than those shown. The fact that at higher pressures the voltage necessary to maintain type A discharge was higher than that necessary to maintain type B explains why it was not always possible to obtain the second discontinuity in the current in the previous part of the work, though in some cases the increase in potential across the tube due to the change in current through the resistance ( $R_2$ ) was sufficient to make it possible to maintain type A

Fig. 3.



discharge after type B disappeared. Curve I. shows that the two types were scarcely distinguishable at the shorter distances and a region of pressures.

The results given in fig. 4 were obtained with a constant filament current, and give the relation between the least maintaining voltage  $V_m$  and the distance between electrodes—Curve I. when the pressure was such that the positive column was uniform with a tube 2.8 cm. in diameter, and curve II. when the positive column was striated with a tube 4.0 cm. in diameter.

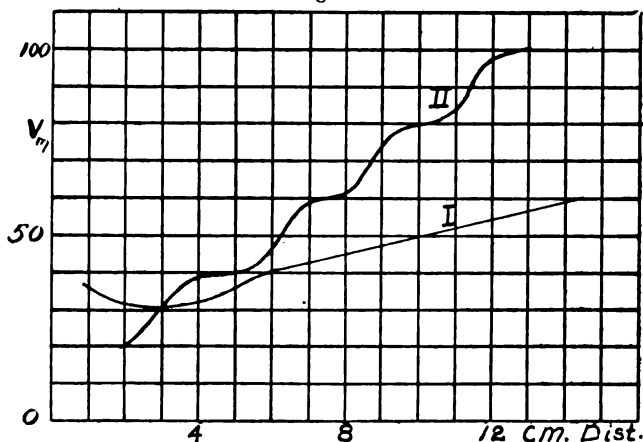
These results are not in accordance with those obtained by Gibson and Noyes\*, who found that the least voltage at which it was possible to maintain the luminous discharge in hydrogen was a multiple of 30.9 volts. The present work shows maintaining voltages lower than those obtained by Gibson and Noyes, though the experimental conditions appear to have been similar to theirs. It is therefore possible that

\* Journ. Amer. Chem. Soc., Oct. 1922.

they did not reach absolute minimum values of  $V_m$  in all cases.

A possible explanation of the results given here may be found on the assumption that the necessary condition for a discharge is that the electron must have sufficient energy to ionize at its first impact. If this condition is to be satisfied, and the potential distribution in Geissler tubes considered, it is evident that the voltage necessary to maintain the discharge must increase with the distance between the electrodes. Consider the case where the anode was situated in the positive column. The least voltage for any distance was found at gas pressures such that the positive column was uniform. Thus the least maintaining voltage  $V_m$  should be

Fig. 4.



expressible, for any position in the positive column, by an equation of the form  $V_m = V_d + XV$ , where  $V$  is the uniform potential gradient of the positive column,  $V_d$  the potential between the cathode and the head of the positive column, and  $X$  the distance of the anode from the head of the positive column. If, on the other hand, the distance between electrodes is such that the anode is situated in the Faraday dark space, when the discharge breaks no such simple expression for  $V_m$  could be found, for in that region the potential gradient is not uniform. The same would be expected to be true at pressure conditions such as to give a striated positive column, as in this case the potential gradient of the positive column is not uniform, but approximates more or less to a periodic value\*. These relations seem to have held in results shown in fig. 4, where Curve I. represents the

\* Thomson, Phil. Mag., Dec. 1921.

relation between distance and  $V_m$  when the positive column was uniform, while Curve II. represents the same when the positive column was striated. (The filament temperature was kept constant throughout the whole set of observations shown in fig. 4.) The potential difference between successive striations is seen to have been slightly more than the ionizing potential of hydrogen, the excess being attributed to the resistance of the gas.

### PART III.—*Observations on $V_m$ in mercury vapour.*

The only change in apparatus for this part of the work was the addition of a small side tube, in which the mercury was put to get the required pressure. This tube was immersed in a constant temperature bath, and the main tube enclosed in an electric furnace and kept at a temperature slightly higher than that of the mercury in the side tube. The tube was at all times left open to the evacuating system to remove impurities arising from the discharge, as were found by Yao in his work on low-voltage arcs in mercury. This procedure should not affect the pressure in the tube, as the pressure gradient should be taken up in the small tube communicating with the evacuating system.

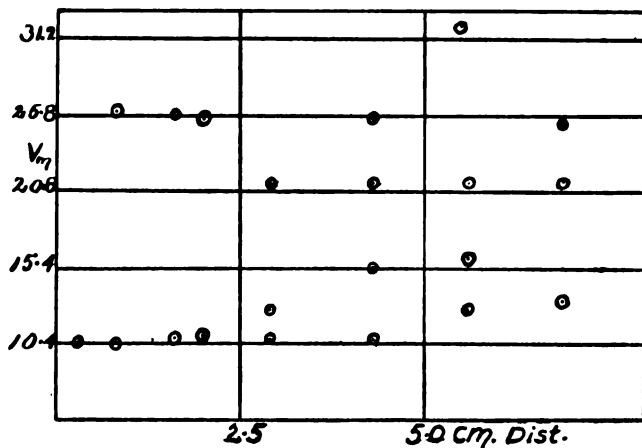
The results of this work so far have not been entirely satisfactory, which is due, probably, to slight variations in temperature of the tube during the course of a run. They appear to indicate, however, that the least maintaining voltage for the discharge in mercury may be expressed by equations of the form  $V_m = nV_i + V_r$  or  $V_m = nV_i$ , where  $V_i$  is the ionizing potential of mercury 10.4 volts, and  $V_r$  the first radiating potential 4.9 volts,  $n$  being an integer. Gibson and Noyes\* in their work found the second relation to hold, but did not find cases in which the first applied.

The results are shown in fig. 5, where the different voltages at which abrupt changes in the current occurred are plotted for different distances. Taking any distance given in the figure, it will be seen that there were several voltages at which the current changed abruptly, also that these voltages seem to obey quite well the relations stated above. At greater distances, however, it will be observed that the lowest point shown on the figure did not obey this relation so well. In the case of these points the current was very small and the luminosity in the tube correspondingly weak, so it was possible that this type of discharge might have been the same as has been called type A in hydrogen. At the pressure at which the results recorded were obtained, the

\* *Loc. cit.*

discharge showed a striated positive column, but it was impossible to determine whether it was still striated when the final break occurred.

Fig. 5.



### Summary.

(1) In Geissler tubes fitted with hot cathodes there were two discontinuous changes in the current as the voltage across the tube is increased, these changes being associated with the appearance of two types of luminous discharge. At short distances between the electrodes, however, one of these disappears, and the conditions of the low-voltage arc, stimulated by the emission from a hot cathode, appeared.

(2) The behaviour of the two types of discharge under various changes in conditions was not the same, although the spectra appeared to differ only in intensity.

(3) The least voltage at which it was possible to maintain a discharge was not found to bear any simple relation to the ionizing potential of hydrogen, a reason for which has been offered.

(4) The voltages at which discontinuous changes in the current with mercury vapour occurred were found to be multiples of the ionization potential or these multiples plus the first radiating potential.

In conclusion, the writer wishes to express his appreciation to Professor K. T. Compton, under whose supervision this work was done, for his unfailing interest and many valuable suggestions during the course of this investigation.

Palmer Physical Laboratory,  
Princeton University.



LVII. *On the Physical Properties of Elements at High Temperatures.* By MEGH NAD SAHA \*.

THE investigation of the physical properties of elements at high temperature is at present exciting a considerable amount of interest, on the theoretical as well as on the practical side. The present paper is the outcome of certain investigations undertaken by the author, which were withheld from publication because no positive result was obtained. But in view of the recent works, it appeared advisable to give publicity at least to certain points which appear to have been rather lightly passed over by recent workers.

Let us picture to ourselves a quantity of gas, elementary or compound, which is being raised to higher and higher temperatures. The physical changes occurring in the mass under such an increasing stimulus have been discussed in previous papers †. It has been shown that the gas will become luminous, will emit its characteristic lines—principal lines, sharp and diffuse lines, Bergmann lines—and ultimately will be ionized. The problem before us is: (1) to determine the statistical distribution of the atoms in the various quantum orbits, and from this to deduce the intensity of the different lines of the characteristic spectrum; (2) to determine the electrical and optical properties of such a mass of ionized gas.

The method which the present writer followed was purely thermodynamical. It consisted in the application of a form of the law of reaction-isochores, which was originally developed by Nernst for the study of the dissociation-equilibria of gaseous compounds from their physical properties, to the problem of ionization. The same method was followed in the extension of the method to mixtures of different elements by H. N. Russell ‡. But in this, as in other cases, thermodynamics lead us rather blindfolded to the goal, and do not enable us to see the details of the intervening stages.

A very powerful method has recently been developed by Messrs. Darwin and Fowler § in a number of important papers published in the *Phil. Mag.* and *Proc. of the Camb. Phil. Soc.* Probably with the aid of this method the problem is

\* Communicated by the Author.

† M. N. Saha, *Proc. Roy. Soc. Lond.* May 1921. *Phil. Mag.* vol. xli. p. 267 *et seq.*, see particularly p. 274.

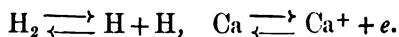
‡ Russell, 'The *Astrophysical Journal*,' vol. lv. p. 143. Milne, 'The *Observatory*,' vol. xlv. Sept. 1921.

§ Darwin & Fowler, *Phil. Mag.* vols. xlv. & xlv. *Proc. Camb. Phil. Soc.* vol. xxi. parts 3 & 4.

brought much nearer to solution, but it seems that there are a number of important points on which the authors have not laid sufficient stress. The first point to which I wish to call attention is that "no theory of dissociation-equilibrium can be said to be complete unless it takes account of the mutual interaction between matter (atoms) and radiant energy, because at high temperatures, exchange of energy takes place mainly by radiation, and only to a slight extent by collision."

*Binding of an Electron with a Proton ( $H^+$ ).*

To make the above point clear, we shall consider the simplest case conceivable—namely, the binding of an electron with a proton to form an H-atom. This case can rightly be called the simplest, because, thanks to the Bohr theory, all the possible states of combination are known, and the dynamics can be handled with easy mathematics—advantages which are not present in such cases as the reactions



Let us first treat the dynamical part. An electron starts from infinity with velocity  $v$ , and passes past a stationary proton. What are the conditions that this will be captured by the proton? A little consideration will show that as long as the energy of the system remains conserved, the electron will describe an hyperbola with the proton as the inner focus, and thus, after wheeling round the proton, will pass off to infinity. In other words, it can never be captured by the proton and lodged in one of the stationary Bohr orbits

(having the energy  $-\frac{Nh}{n^2}$ ) unless the system loses the energy  $\frac{1}{2}mv^2 + \frac{Nh}{n^2}$  presumably by radiation.

From physical ground, it seems to be fairly well established that such a process actually takes place in nature in all cases of ionization, giving rise to a continuous spectrum beginning from the limit of the series lines. In the case of hydrogen, the continuous spectrum was first detected by Huggins during the observation of the eclipse spectra, and was confirmed by Evershed. The explanation cited above is due to Bohr. (See 'Atombau und Spektralanalyse,' p. 547, 3rd edition.)

But the dynamical interpretation of this process from the standpoint of quantum mechanics is far from satisfactory, as

has been pointed out by Nicholson\* in a recent paper. Eddington† has thrown out the suggestion that during its orbital motion the electron loses energy by radiation just as an accelerated electron would do according to the classical theory. But here we are treading on rather dangerous ground, as the satisfactory working out of the suggestion means nothing less than the discovery of the linkage between the classical theory and the quantum theory.

In the case of hydrogen, the continuous spectrum has been observed at the limiting frequency of the Balmer series (quantum orbit 2, or  $2_1$ ), but this is owing to the fact that observations do not probably extend up to the limit of the Lyman series. In the case of the alkali elements, the continuous spectrum has been observed extending towards the short wave-length side from the limiting frequency of the principal series. These facts are very decisive in favour of the view that combination of an ionized atom with an electron is always accompanied by liberation of energy in the form of continuous waves of light.

*The Statistical part; deduction of the Law of Reaction-isochore for the Ionization of the H-atom.*

This part has been worked out by Fowler, but before taking up his method of deduction, I shall give another deduction based on the older methods, because this may serve to bring out the details of the case in a more intelligible manner.

The problem which we are discussing is only a special case of the general problem of association of particles and dissociation of compound particles which was first treated from the standpoint of the kinetic theory by Boltzmann, Natanson, and J. J. Thomson about thirty years ago. A masterly discussion is given in Jeans's 'Dynamical Theory of Gases,' p. 213 *et seq.*, 3rd edition. This treatment is applicable, of course with some alteration, to the combination of protons and electrons.

Suppose we have a system consisting of  $2\nu_1$  particles of type A, and  $\nu_2$  particles of type  $A_2$  formed by the combination of two particles A. Let  $\nu = 2(\nu_1 + \nu_2)$ : i. e.,  $\nu$  is the total number of particles if there be no aggregation at all.

Then Jeans shows that an encounter between two particles of type A can never result in an association unless the quantity  $\frac{1}{2}mv^2 + 2\psi$  (where  $2\psi$  = mutual potential energy of the particles,  $v$  relative velocity of the two particles) assumes a negative value. According to Jeans, "this might be effected by collision with a third molecule [*it is not at all*

\* Nicholson, Phil. Mag. vol. xlv. p. 193 (1922).

† Eddington, Monthly Notices R. A. S. vol. lxxxiii p. 43.

clear how], or possibly, if  $\frac{1}{2}mv^2 + 2\psi$  were small at the beginning of the encounter, sufficient energy might be dissipated by radiation for  $\frac{1}{2}mv^2 + 2\psi$  to become negative before the termination of the encounter."

Jeans continues: "we may leave the consideration of this second possibility on one side for the present, with the remark that if this were the primary cause of aggregation, we should no longer be able to use the equations with which we have been working, since they rest upon the assumption of conservation of energy."

The simplest illustration of association is the binding of a proton ( $H^+$ ) with an electron. As has been already shown, here it is not possible to leave on one side the action of radiation, for that will be tantamount to staging the play of Hamlet without Hamlet's part; for physical evidences decisively prove that radiation is emitted in all cases of the binding of an ionized atom with the electron. Similarly, absorption of radiation is essential for the splitting up of an atom  $M$  into  $M^+$  and  $e$ .

In spite of rather uncertain knowledge regarding the rôle of radiant energy in these processes, Boltzmann deduced a formula on the assumption that potential energy exists between two molecules (here we should say between  $H^+$  and  $e$ ), when the centre of the second ( $e$ ) lies within a sensitive region surrounding the first ( $H^+$ ). With this assumption, Boltzmann obtains a formula (formula 503 of page 199, 3rd edition, Jeans's 'Dynamical Theory of Gases') which, with a slight change in notation, can be put in the form

$$\frac{x^2}{1-x^2} P = \frac{kT}{4\omega} e^{-\frac{U}{kT}}, \quad \dots \quad (A)$$

where  $\omega$  = volume of the sensitive region.

Comparing this with the formula for reaction-isobar derived by me, viz.

$$\log \frac{x^2}{1-x^2} P = -\frac{U}{RT} + \frac{5}{2} \log T + \log \left\{ \frac{(2\pi m)^{3/2} k^{5/2}}{h^3} \right\}, \quad (B)$$

we find that

$$\omega = \frac{1}{4} \left( \frac{h^2}{2\pi m k T} \right)^{3/2}, \quad \dots \quad (C)$$

or  $r$ , the radius of the sensitive layer,

$$r = \left( \frac{3}{16\pi} \right)^{1/3} \left( \frac{h^2}{2\pi m k T} \right)^{1/2};$$

i. e., the radius of the sensitive layer varies as

$$\frac{2.95 \times 10^{-6}}{T^{1/2}} \text{ cm.}$$

*Fowler's work on the Reaction-isobar of the  
Ionization of the H-atom.*

We now turn to the very interesting and novel method of deriving the law of reaction-isochore by Messrs. Darwin and Fowler. Fowler deduced the law

$$\log \frac{x^2}{1-x^2} P = -\frac{U}{RT} + \frac{5}{2} \log T + \log \left\{ \frac{(2\pi m)^{3/2} k^{5/2}}{h^3} \right\} + B(T), \quad \dots (D)$$

which differs from my formula in the term  $B(T)$ .

In the thermodynamical way of derivation of the reaction-isochore the roll of radiation is left obscure. The same remark may be applied to Fowler's method of deduction, as has been admitted by Fowler in the following passage (page 13, *Phil. Mag.*, Jan. 1923):—

“In conclusion, a possible objection may be raised to all the reasoning on which these results are based—namely, that it ignores radiation, whereas in fact a change of quantum state in the molecule probably seldom or never occurs without the emission or absorption of the appropriate radiation.”

I would like to add to this passage: Likewise ionization of the H-atom, or association of the proton ( $H^+$ ) and the electron, seldom or never occurs without the absorption or emission of the appropriate radiation.

Fowler continues: “It is, however, perfectly possible to include the temperature radiation in the statistical discussion, as has been shown elsewhere.”

In the passage referred to above (*Proc. Camb. Phil. Soc.* vol. xxi. p. 263), Messrs. Darwin and Fowler, starting from the partition-function of a Planck line-vibrator, have given an interesting method of deduction of the laws of black-body radiation; but I find it difficult to agree with the view that this includes the temperature radiation in the statistical discussion. They have treated radiant energy as the energy of a single system, the æther, and neglected matter altogether, except through that somewhat shadowy medium, the Planck line-vibrator. But the problem before us is to find out the exact nature of exchanges between Bohr vibrators and radiant energy which has not been covered in the above treatment.

We now come to the consideration of the term  $B(T)$  in Fowler's formula.

The term  $B(T)$  represents the energy distribution amongst the Bohr vibrators, and is simply another form of the partition function for the internal energy of the Bohr atom. According

to Fowler this partition function  $b(\vartheta)$  is given by

$$b(\vartheta) = \sum_{n=1}^{\infty} n(n+1) \vartheta^{\chi(1-\frac{1}{n^2})}$$

[equation 7·22, p. 20, Phil. Mag., Jan. 1923],

where

$$\vartheta = e^{-\frac{1}{kT}}, \quad \chi = Nh, \quad N = \text{Rydberg number.}$$

As Fowler himself points out, this is a divergent series, and cannot therefore be regarded as solution of the problem. But his suggestion, that the series ought to be cut down to a finite number of terms because the higher terms correspond to orbits with large radii, does not seem to lead out of the difficulty, as imagined by him. For whatever may be the origin of the higher Balmer lines, they are not unknown, nor do they require very special physical conditions for their development. For example, Mitchell could detect 35 lines of the Balmer series within the lower 2000 kms. of the solar chromosphere, and Wood has recorded 21 of them in his vacuum tubes. The difficulties of dealing with the higher orbits on the quantum conditions

$$\oint p \delta q = nh$$

also been emphasized by Nicholson.

To me, the divergence of Fowler's formula (7·22) appears to be a clear indication that Bohr's hypothesis regarding the weight factor of the higher quantum orbits, viz.  $p_n = n(n+1)$ , is wrong. In fact, any consideration \* which tends to assign to the larger quantum orbits larger probability seems to be opposed to physical facts †.

### *Electrical and Optical Properties of Ionized Gases.*

A mass of gas at ordinary temperatures, and not subjected to ultra-violet light, Röntgen light, or any other familiar ionizing agent, possesses no electrical conductivity, because there are no free carriers of electricity present. But if the gas be raised to a high temperature and partially ionized, it will acquire considerable conductivity.

This was pointed out by me in previous papers ‡, and the non-success of previous experiments, as those of J. J. Thomson

\* For example, Planck, *Berl. Sitzungsberichte*, p. 407, 1915.

† M. N. Saha, *Phil. Mag.* vol. xli. p. 274.

‡ "On the Ionization of Gases by Heat," by M. N. Saha and P. Günther, *Journ. Dept. Sci. Calcutta University*, vol. iv. See also A. A. Noyes and H. A. Wilson, *Ast. Journ.* vol. lvi. p. 21.

and McLennan, on the electrical conductivity of mercury vapour were discussed in detail. It was shown that these investigators chose a substance which has too high an ionization-potential (10·45 volts), and hence at the temperature employed by them the mass of gas (mercury-vapour) remained practically unionized.

Cæsium is the element having the lowest ionization-potential, and hence I pointed out that this is the element with which success can be expected at temperatures available in the laboratory. Some preliminary experiments undertaken by me at Prof. Nernst's laboratory at Berlin confirmed these expectations. At 1250° C., Cs-vapour was found to have a specific resistance of only 50 ohms, which increased to about 100 ohms when the temperature was lowered to 1050° C. The current could be measured with a milliammeter with a voltage difference of 1 to 2 volts across the ionization-cell containing Cs-vapour, and obeyed Ohm's law throughout the range 1 to 6 volts. These figures are very rough, but they, taken along with the figures for Rb and K (which were found to have increasingly higher resistance), completely confirm the view that the ionization potential is the deciding factor in determining the electrical conductivity of heated vapours.

But great difficulty was encountered when I tried to calculate the conductivity from the Drude-Thomson theory. It was felt that if this theory were applicable to any case, it was the present one. But calculations have not answered to this expectation.

Suppose we have a mass of vapour, say of Cs, which is ionized by heat. Let  $n_1$  denote the number of free electrons or Cs<sup>+</sup>-ions per unit volume,  $\lambda_1$  and  $\lambda_2$  the mean free paths,  $u_1$  and  $u_2$  the average velocities of the electrons and the positively-charged particles respectively. Then, according to the Drude-Thomson theory, the conductivity

$$\sigma = \frac{n_1 e^2}{6kT} (\lambda_1 u_1 + \lambda_2 u_2). \quad \dots \quad (E)$$

According to the kinetic theory of gases, if we have a mixture of gases of different kinds (1, 2, ...,  $r$ ,  $s$ , ...), then the mean free path  $\lambda_r$  of any particular type  $r$  is given by the expression

$$\frac{1}{\pi \lambda_r} = \sum_{s=1} n_s A_{rs}^2 \sqrt{1 + \frac{m_r}{m_s}}. \quad \dots \quad (F)$$

[see Jeans, 'On the Dynamical Theory of Gases,' p. 268],

where  $A_{rs} = A_r + A_s$ ; the sum of the radii of the “ $r$ ” and “ $s$ ” particles,  $n_s$  is the concentration of the “ $s$ ” particle.

In the present case we have to deal with Cs,  $\text{Cs}^+$ , and  $e^-$ , Cs-particles of course including different types distinguished by the quantum orbits ( $n_k$ ). Let us neglect all the higher orbits and retain only the fundamental orbit ( $1_1$ ), a step which will not be acceptable to many, but which is difficult to avoid or improve under the present state of our knowledge. Then

$$\frac{1}{\pi\lambda_1} = n \frac{A^2}{4}, \quad \frac{1}{\pi\lambda_2} = nA^2 \sqrt{2}, \quad \frac{1}{\pi\lambda} = nA^2 \sqrt{2}.$$

Assuming that the degree of ionization is small (i.e.,  $n_1$  is small compared with  $n$ , the concentration of Cs-atoms),  $A$  denotes the radius of Cs-atom, then  $\lambda_1 = 4\sqrt{2}A$  (a well-known result) and

$$\lambda_2 = \lambda, \quad u_1 = \sqrt{\frac{3kT}{m}}, \quad u_2 = \sqrt{\frac{3kT}{M}}.$$

Since  $\text{Cs}^+$  is  $1836 \times A$  (atomic weight) times heavier than  $m$ , we see that  $u_2$  is negligible compared with  $u_1$ . This only means that the conductivity is mainly due to electrons.

We have now

$$\sigma = \frac{2\pi e^2}{\sqrt{3mkT}} \frac{1}{A^2} x, \quad \dots \dots \dots (E')$$

where  $x$  = fraction ionized.

Now “ $x$ ” can be calculated from the formula of reaction-isochores.

$$\text{We have} \quad \frac{x^2 P}{1-x^2} = \frac{(2\pi m)^{3/2} k^{5/2}}{h^3} T^{5/2} e^{-\frac{U}{RT}}. \quad \dots \dots (B')$$

and

$$P = n(1+x)kT,$$

or

$$\frac{x^2}{1-x} = \left( \frac{2\pi mkT}{h^2} \right)^{3/2} \frac{1}{n} e^{-\frac{U}{RT}} = \frac{B}{n}; \quad \dots \dots (B'')$$

therefore

$$x = \sqrt{\frac{B}{n}}, \quad \text{or} \quad \frac{B+n}{B+2n},$$

according as “ $n$ ” is large, or “small” compared with “ $B$ .”

The second case will never arise, unless we have to deal with a case of very high temperature and very low pressure (e.g., in the giant stars).



Hence the conductivity

$$\sigma = \frac{(2\pi)^{3/2}}{\sqrt{3}} \frac{(mkT)^{1/4}}{h^{3/2}} e^2 \exp\left(-\frac{U}{2RT}\right) \frac{1}{\sqrt{n}} \dots (E'')$$

The only thing to notice about this complicated expression is that  $\sigma$  varies inversely as  $\sqrt{\text{concentration}}$ .

This is an unexpected result, and is not corroborated by my experiments, for I found that the conductivity diminishes gradually as the vapour-content diminishes. *A priori*, it seems rather paradoxical that the conductivity will vary as  $1/\sqrt{n}$ .

Therefore, either we cannot calculate the percentage of ionization from the law of reaction-isobar at very low concentrations, or the Drude-Thomson theory of conduction which makes the conductivity proportional to the percentage of ionization, and not to the total number of ionized particles present, fails to give us a true picture of the phenomena.

#### *The Mean Free Path of an Electron in a mass of Ionized Gas.*

The cause of this failure is not far to seek. We have to calculate the "free life" of an electron in a mass containing normal atoms of Cs, atoms with higher quantum orbits, and  $\text{Cs}^+$ -particles. The mean free path, as deduced in formula (F), is based upon the idea of elastic collisions, which is rather the opposite of what actually takes place. As has been explained in the previous sections, in representing the complicated reactions which occur when a free electron encounters a  $\text{Cs}^+$ -atom, or a Cs-atom in normal or higher orbits, the idea of elastic collision is of no avail, the exchanges of energy through radiation must be taken into account.

The same considerations apply to the optical properties of ionized gases discussed by Prof. J. Q. Stewart in a letter to 'Nature,' Feb. 10, 1921, but the discussion is deferred to a future date.

[*Note* : Since the above paper was written, I have been made acquainted, through the courtesy of Messrs. Fowler and Darwin, with a paper by them "On the Intensities of Absorption Lines in Stellar Spectra, etc.," published in the M. N. R. A. S. vol. lxxxiii. p. 403. In this paper Fowler and Milne have given an interesting method of deducing the pressure in the reversing layer by applying a theory of

maximum intensities of subordinate lines which they have worked out. It must be admitted that the idea is pregnant with great possibilities, and would lead to important results if the correct partition function  $b(\mathfrak{S})$  can be discovered. But Fowler and Milne have used the function  $b(\mathfrak{S})$  mentioned above, which, being a divergent series, is rather unconvincing.—M. N. S.]

LVIII. *On the Colour of the Sea.* By K. R. RAMANATHAN, M.A., Assistant Lecturer in Physics, University College, Rangoon, Burma\*.

### 1. Introduction.

**I**N a recent paper †, Prof. C. V. Raman has put forward the theory that the deep blue colour characteristic of the larger part of ocean waters is due to the molecular scattering of light in water, and supported it by calculations of the intensity and quality of the light returned from deep water. He has shown that pure, dust-free water scatters light in accordance with a formula originally deduced by Einstein for the critical opalescence of fluids, and that molecular scattering by itself without the aid of any extraneous agency is sufficient to account for the return of a part of the incident light. The following investigation was undertaken in order to test how far actual sea-water comes up to the ideal dust-free condition, and to find how the waters in seas showing different colours vary from one another.

### 2. Theoretical Discussion.

Preliminarily, it is useful to consider what intensity and colour we should expect from a *perfectly absorptionless* dust-free ocean of infinite depth. In such a case, the diminution of intensity of light in its passage through the medium would be wholly accounted for by molecular scattering. Since there is no transformation of the incident energy, it would be entirely thrown back, and the returned light would be of the same quality as the incident ‡. Since the scattering coefficient varies inversely as the fourth-power of the wave-length, the depth of the medium responsible for the return of a certain percentage of blue light would be smaller than that responsible for the return of the same

\* Communicated by Prof. C. V. Raman, M.A., D.Sc.

† C. V. Raman, Proc. Roy. Soc. A, vol. ci. p. 64 (1922). See also 'Molecular Diffraction of Light,' Calcutta University Press, 1922, chapter v.

‡ *Vide* Schuster, 'Theory of Optics,' Second Edition, p. 271.

percentage of red light. Selective absorption, however, would modify the condition of affairs. The light of those wave-lengths for which the medium exercises a selective absorption would be gradually diminished in intensity as the light penetrates into the medium, and if the absorption is at all considerable, there would be very little of these radiations returned. Now, water is known to exercise a selective absorption in the red which gradually decreases as we proceed into the region of shorter wave-lengths. The most extensive measurements of absorption coefficients for water that we possess are those of Count Aufsess\* between wave-lengths  $658\ \mu\mu$  and  $494\ \mu\mu$ . Recently, W. H. Martin† has measured the absorption coefficients of water repeatedly distilled *in vacuo* for the mercury lines  $578\ \mu\mu$ ,  $546.1\ \mu\mu$ , and  $435.8\ \mu\mu$ . As has been pointed out by Martin, there is an error in Aufsess's measurements, as he neglected to take into account the loss of light on reflexion at the glass surfaces at the ends of the absorption-tube. However, considering the length of tube which Aufsess employed (5.5 metres), the relative error involved is not large in the region of the red where the absorption is large. We shall therefore adopt Aufsess's values for the absorption coefficients in the red. In Table I. are shown the experimental values of the extinction coefficient  $\gamma$ , defined by  $I = I_0 e^{-\gamma x}$ , where  $I_0$  is the intensity of a parallel beam of incident light, and  $I$  is the intensity after traversing a thickness  $x$  of water. In the fourth column are shown the values of the extinction coefficients, if the extinction were due *solely* to molecular scattering. These are calculated according to the formula

$$\alpha = \frac{8\pi^3}{27} \frac{RT\beta}{N\lambda^4} (\mu^2 - 1)^2 (\mu^2 + 2)^2 \dagger.$$

\* Count Aufsess, *Ann. der Physik*, vol. xiii. (1904).

† W. H. Martin, *Journ. Phys. Chem.* xxvi. p. 471 (1922).

‡ *Vide* C. V. Raman, *loc. cit.* and 'Molecular Diffraction of Light,' chapter iv. p. 52.

This is derived on the assumption that the light scattered in a direction perpendicular to the incident beam is perfectly polarized. As a matter of fact, the transversely scattered light shows a defect in polarization. In addition to the polarized "Einstein scattering," there is an additional scattering due to the anisotropy of the molecules, which for the most part is unpolarized. If we take the latter also into account, the formula for the coefficient of extinction becomes

$$\alpha = \frac{2\pi^3}{9} \frac{RT\beta}{N\lambda^4} (\mu^2 - 1)^2 (\mu^2 + 2)^2 \left\{ \frac{4}{3} + \frac{r}{1-r} \right\},$$

where  $r$  is the ratio of the weak component to the strong in the transversely scattered light, and the values of the extinction coefficients come out to be  $8.2 \times 10^{-6}$ ,  $1.08 \times 10^{-5}$ ,  $1.38 \times 10^{-5}$ ,  $1.76 \times 10^{-5}$ , and  $5.0 \times 10^{-6}$  for the wave-lengths given above.

TABLE I.

Wave-length.	Absorption coefficient.	Author.	Extinction coefficient due to scattering alone.
658.....	$3.2 \times 10^{-3}$	Aufsess.	$7.5 \times 10^{-6}$
612.....	$2.33 \times 10^{-3}$	Aufsess.	$9.9 \times 10^{-6}$
578.....	$6.4 \times 10^{-4}$	Martin.	$1.3 \times 10^{-5}$
546.1.....	$3.4 \times 10^{-4}$	Martin.	$1.6 \times 10^{-5}$
435.8.....	$1.2 \times 10^{-4}$	Martin.	$4.3 \times 10^{-5}$

In the red, yellow, and green, up to  $546 \mu\mu$ , practically the whole of the extinction is due to absorption, while in the blue and the violet, scattering takes away an appreciable part. The intensity of the incident radiation is reduced to one-half at a depth of approximately 2 metres for  $658 \mu\mu$ , 10 metres for  $578 \mu\mu$ , 20 metres for  $546 \mu\mu$ , and 60 metres for  $435.8 \mu\mu$ . Taking primary scattering alone into account and considering the directions of incidence and observation to be vertical, the total observed brightness due to an infinite depth of water can be easily shown to be  $B/\gamma\lambda^4$ \*, where the scattering coefficient in a transverse direction has the value

$$B = \frac{\pi^2}{18} \frac{RT\beta}{N\lambda^4} (\mu^2 - 1)^2 (\mu^2 + 2)^2.$$

We can now see why the returned light should be specially deficient in the red, yellow, and green. The increase in absorption goes hand in hand with the decrease in scattering, and the two together serve practically to eliminate the longer wave-lengths. The following Table gives the course of values of  $B/\gamma\lambda^4$  :—

$\lambda$ in $\mu\mu$ .	658.	612.	578.	546.	436.
$B/\gamma\lambda^4$ .....	$1.4 \times 10^{-4}$	$2.5 \times 10^{-4}$	$1.2 \times 10^{-3}$	$2.8 \times 10^{-3}$	$2.1 \times 10^{-2}$

In order to obtain the resultant colour of the sea, we have only to compound the effects of different wave-lengths in their proper proportions. The intensities for the different wave-lengths throughout the visible spectrum can be obtained

\* C. V. Raman, *loc. cit.* If the anisotropic scattering is also taken into account this would become  $B(1+r)/\gamma\lambda^4$ .

by the above formula, and their colour effects expressed in terms of the spectrum colours  $630\cdot2\ \mu\mu$ ,  $538\cdot1\ \mu\mu$ , and  $456\cdot9\ \mu\mu$ , using the values given by the late Lord Rayleigh in his paper on "The Colours of Thin Plates"\*. The resultant colour is found to have the composition  $1\cdot56 \times 10^{-3}$  red,  $2\cdot49 \times 10^{-2}$  green, and  $9\cdot53 \times 10^{-2}$  violet, and approaches the spectrum colour  $475\cdot0\ \mu\mu$ , being very near the indigo of the second order in the colours of thin plates. The inclusion of secondary scattering would reduce the effective depth of the sea from which the scattered light returns; it would also serve to further diminish the intensities of the red and yellow, for which the absorption is strong.

It is obvious that the presence of any dissolved matter giving rise to extra absorption in any particular region of the spectrum would cause a corresponding diminution of the intensity of the returning light in that region of the spectrum.

Let us now consider the effect of suspended matter. It would give rise to an additional scattering, and hence the depth to which the light would penetrate would get reduced. If the particles are small in comparison with the wave-length, the scattering would still be proportional to  $\lambda^{-4}$ . If present in small quantities, there would be little effect on the characters of the returned light, but if present in larger quantities, there would be less chance for the absorptive properties of the medium to have their full play, and as a consequence, the light would be more mixed with the longer wave-lengths, and the blue colour of the sea would tend to get less saturated. As the particles get larger in comparison with the wave-length, the scattering in the direction of primary propagation will be specially favoured, and also, instead of being proportional to, it would tend to be independent of the wave-length. Since the light of longer wave-lengths can return by other means than molecular scattering, their relative proportion in the light returned would increase more and more as the quantity of suspended matter increased, and the sea would get greenish blue, green, whitish green, and finally white. However, as we shall see, when the quantity of matter is not large, the light scattered against the direction of the incident light is but an insignificant fraction of that scattered in the direction of the incident light.

\* Lord Rayleigh, 'Scientific Papers,' vol. ii. table i. p. 503.

III. *Examination of Light scattered by Sea-water.*

Samples of sea-water were collected in carefully cleaned stoppered bottles from the Bay of Bengal in two voyages between Calcutta and Rangoon from places where the sea exhibited different colours varying from deep indigo to green. The bottles were securely placed in a galvanized-iron wire cage tied to the end of a wire, and the cage was thrown into the sea from the lower deck of the ship near the bow. The bottles were rinsed out with the sea-water five or six times before each sample was finally collected. The colour of the sea at the time was also noted. In observing the proper colour of the sea, a nicol is helpful in abolishing sky-reflexion, as has been pointed out by Raman.

The scattering of light by the different specimens was examined by concentrating a beam of sunlight at the centre of each bottle in a dark room. The back surfaces of the bottles were painted black, in order to be better able to see the tracks. Table II. gives the details regarding the scattering in different specimens. The intensities of the transversely scattered light given in the last column are expressed in terms of that in dust-free distilled water.

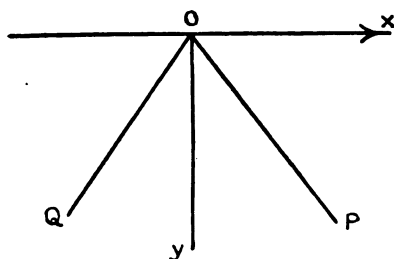
TABLE II.

Specimen No.	Date and time of collection.	Approximate position of ship at time of collection.	Colour of Sea.	Appearance of transversely scattered light.	Intensity of transversely scattered light.
A .....	1.10.22. 10.30 A.M.	...	Indigo.	Indigo with visible particles.	1.68
B .....	4.11.22. 8 A.M.	Lat. 19° 40' N. Long. 90° E.	Greenish blue.	Blue—Few visible particles.	1.4
C .....	4.11.22. 11.15 A.M.	Lat. 19° 10' N. Long. 90° 30' E.	Deep blue.	Indigo—A few large particles.	1.5
D .....	4.11.22. 4 P.M.	Lat. 18° 30' N. Long. 91° E.	Indigo.	Indigo—A few large particles.	1.5
E .....	5.11.22. 7.30 A.M.	...	Greenish.	Blue with large thin flakes of something floating.	1.65
F .....	5.11.22. 11.40 A.M.	Lat. 15° 30' N. Long. 94° 15' E.	Green.	Bluish white—Motes visible.	1.6 Blue. 2.0 Red.

The colour of the transversely scattered light in specimens A, C, and D approached that of dust-free distilled water. The intensity of the transversely scattered light from A was compared with that from dust-free distilled water, by sending a concentrated beam of light through the two bottles in succession and making use of an Abney rotating disk-photometer for equalizing the intensities. Correction was made for the loss of light on reflexion at the glass surfaces. In the case of the other specimens, the comparisons were made by inserting perpendicularly in the path of the stronger beam a number of thin, selected microscope slides, so as to equalize the apparent brightnesses.

When the direction of observation was OP instead of Oy, the suspended particles were much more in evidence

Fig. 1.

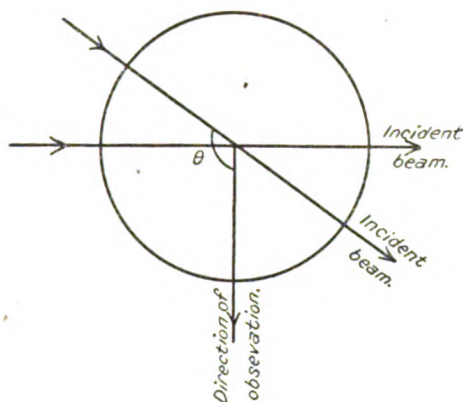


and the colour was more reddish. On the other hand, in the direction OQ, the particles were less conspicuous and the colour even more saturated than along Oy. This is what we should expect if the particles are large in comparison with the wave-length. Since, in the case of the sea, we are primarily concerned with the light proceeding backward, we should consider the intensity of the scattered beam in a direction against that of the incident beam. Comparisons of the intensity of scattering in different directions were made by the method indicated below (fig. 2).

Two beams of sunlight were concentrated one above the other at the centre of the bottle by two lenses of the same focal length (nearly 100 cm. and achromatic) in directions making a definite angle with each other. The scattering was observed in a direction at right angles to one of the beams, and the apertures of the lenses were adjusted by suitable shutters so that the tracks appeared of equal intensity. The inverse ratio of the areas of the apertures

gives the ratio of the intensities scattered in the two directions. Since the depth of layer contributing to the luminosity is different in the two cases, being proportional to  $\text{cosec } \theta$ , where  $\theta$  is the angle indicated in the figure, the

Fig. 2.



luminosity observed in the direction  $\theta$  was multiplied by  $\sin \theta$  in order to get the effect due to the same thickness of radiating column. Table III. gives the relative intensities of scattering in different directions in specimen A :—

TABLE III.

$S_{\theta}$  = Scattering in specimen in direction  $\theta$ .

$\sigma_{\theta}$  = Scattering in dust-free distilled water in direction  $\theta$ .

$\theta$ .	$S_{\theta}/S_{90^{\circ}}$ .	$S_{\theta}/\sigma_{90^{\circ}}$ .	$\sigma_{\theta}/\sigma_{90^{\circ}}$ .
$30^{\circ}$	1.12	1.88	1.60
$45^{\circ}$	0.91	1.53	1.40
$60^{\circ}$	0.87	1.46	1.20
$90^{\circ}$	1.00	1.68	1.00
$120^{\circ}$	2.54	4.26	1.20
$150^{\circ}$	5.5	9.2	1.60

The values in the fourth column are calculated on the assumption that the scattering by a pure, dust-free liquid in a direction  $\theta$  is given by  $\sigma \left( 1 + \frac{1-r}{1+r} \cos^2 \theta \right)$ , where  $\sigma$  is the scattering in a direction perpendicular to the incident beam. It will be seen that in the particular specimen of sea-water, when  $\theta$  is greater than  $90^{\circ}$ , the scattering increases with



increasing values of  $\theta$  at a much more rapid rate than in dust-free water, and that although the transverse scattering is 1.68 times that of dust-free water, the values of the scattering in directions  $30^\circ$  and  $45^\circ$  are not appreciably different from those of pure water. From the progress of values, we may expect that with smaller values of  $\theta$ , the scattering will be practically the same as for dust-free water.

This result is of great importance in its bearing on the colour of the sea. Suspended matter, when present in small quantities, although it considerably increases the total scattering, contributes but little to the scattering against the direction of the incident light. The increase in the total scattering would reduce the transparency of the medium, but so long as the defect of transparency due to this cause is small compared with the absorption proper, the quality and intensity of the returned light would not be much affected by the presence of such matter.

Table IV. gives similar data for specimens B, C, and F. With a view to bringing out the difference in the distribution of scattered light for red and blue, comparisons were made after introducing ruby-red and deep-blue glasses respectively in the paths of the scattered beams.

TABLE IV.

$\theta$ .	$S_\theta/S_{90^\circ}$ .					
	B.		C.		F.	
	Red.	Blue.	Red.	Blue.	Red.	Blue.
$30^\circ$	1.01	1.22	1.06	1.13	0.88	1.03
$45^\circ$	1.10	1.05	1.13	1.13	0.95	1.02
$60^\circ$	0.90	1.00	0.97	0.97	0.83	0.95
$90^\circ$	1.00	1.00	1.00	1.00	1.00	1.00
$120^\circ$	1.65	1.52	1.55	1.60	2.09	1.63
$135^\circ$	3.92	2.45	3.18	2.76	5.05	3.98
$150^\circ$	9.0	6.0	8.3	6.3	16	9.4

It will be observed that in all cases the red gets more and more prominent as  $\theta$  increases.

We shall now examine whether we can find in the varying amount of suspended matter a sufficient cause for the difference in the colour of the seas. For example, the specimen C was collected from a deep blue sea, while specimen B was from a sea which showed greenish blue,

and F from a place where the sea was green. Compared with C, the intensity of scattering in F, although nearly equal for the blue in a transverse direction, is greater by 30 per cent. in the red, and the asymmetry of scattering also is greater. Thus the total scattering of unit volume of specimen F is greater than that of C, and the colour is also much less blue. Both these causes would contribute to a less deep penetration of the light into the medium (relatively more so for longer wave-lengths), and thus the absorption would have less chance of playing its full role, so that the blue, indigo, and violet would be mixed up with a greater proportion of the longer wave-lengths. We should therefore expect the sea to be brighter and of a less saturated blue, but not the distinct green that it actually was. We have therefore to look for some other cause for the green colour. The point is even clearer if we compare the behaviour of B and C. B scatters actually less than C in a transverse direction (nearly 10 per cent. less); and although its track was not indigo like that of C, the asymmetry of scattering was of practically the same order of quantities, and yet the colour of the sea from which it was collected was *greenish blue*.

#### IV. Fluorescence of Sea-Water.

The reason for the difference was found on examining the transversely scattered light from a horizontal track for polarization by means of a double-image prism. When the double-image prism is so oriented as to transmit vertical and horizontal vibrations, the light corresponding to the horizontal vibrations does not actually vanish even in the case of dust-free distilled water \*; but in this case the two beams are of practically the same colour, while in the case of specimens B and F the weaker component was found to be distinctly *greenish*. The contrast came out sharper when the two beams were equalized for brightness by means of a suitably oriented nicol placed behind the double-image prism, and a double thickness of blue glass was introduced in the path of the incident beam. The green was now much brighter than the blue and the colour contrast sharper. This was evidently a case of *fluorescence*.

To make quite sure, the following arrangement was adopted:—In the path of the incident beam were placed a double thickness of cobalt-blue glass with an absorption cell

\* W. H. Martin, Journ. Phys. Chem. vol. xxiv. p. 478 (1920). C. V. Raman, 'Molecular Diffraction of Light,' chap. iv.

of a solution of potassium permanganate which cut off everything except the extreme blue and violet and a patch in the extreme red. The light was then passed through the sea-water, and the track therein was examined through a prism with its refracting edge horizontal. In addition to the blue and violet, the green was also conspicuously present. Yellow and red were present, but were very faint. Specimen F showed the effect best, B and E came next, and then C and D. The fluorescence was certainly present even in the last two specimens, though it was very weak.

Since the incident light did not contain any ultra-violet, the fluorescence should be excited by the blue and violet. This implies an extra absorption of the blue and the violet. A sea whose water shows the fluorescence would thus appear green, not only because there is a return of green light due to fluorescence, but also as there would be less of the blue and violet returning. As we have seen, that water looks most green which shows the most intense fluorescence, and the water gets more and more towards indigo as the fluorescent material gets less and less.

The transition from the indigo of the deep sea far from land to blue and green may thus be due either to the increase in the amount of suspended matter present, or to the presence of some fluorescent material (most probably organic) which not only causes a return of the green and longer wave-lengths, but also produces a greater absorption of the blue and the violet. The second cause is apparently the more important.

### *V. Summary.*

The paper contains a discussion of Raman's theory of the colour of the sea with observations on the scattering of light by different specimens of sea-water from the Bay of Bengal.

(i.) It is shown that an ocean of pure dust-free water would, owing to the effects of molecular scattering and absorption, return light of an indigo-blue colour. The presence of *small* quantities of suspended matter would not appreciably affect the colour. With increasing quantities of suspended matter the colour would change to bluish, green, greenish white, and white.

(ii.) The transverse scattering from different specimens of sea-water has been compared with that of dust-free vacuum-distilled water. The water from the deep blue sea scatters light of nearly the same colour as dust-free water, and the intensity of the transversely scattered light is also of the same order.

(iii.) The intensity of scattering in different directions from different specimens of sea-water has been studied. The effect of dust is negligible so far as scattering against the direction of the incident light is concerned.

(iv.) The variation of the dust-content is found to be insufficient to explain the changes of the colour of the sea from place to place. An important reason for the colour changes has been traced to the presence of varying amounts of some fluorescent material present in the sea. It is pointed out that this fluorescence also implies a greater absorption in the blue and violet involving a diminution of intensity at this end of the spectrum in the light returned from the sea.

In conclusion, I would express my most sincere thanks to Professor C. V. Raman for his stimulating interest in the work.

Rangoon,  
Feb. 10, 1923.

LIX. *The Motion of Electrons in Hydrogen under the action of Crossed Electric and Magnetic Fields.* By R. N. CHAUDHURI, M.Sc., Ph.D. (London) \*.

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*Introduction.*

IN some previous work (by Richardson and Chaudhuri † ; and Chaudhuri ‡) on the motion of electrons in different gases, it was found that the initial current flowing from the cathode to the anode was diminished by applying a magnetic field perpendicular to the direction of the electric intensity ; and the percentage of the residual current was directly proportional to the pressure (at least well up to  $10^{-2}$  mm.). We drew the conclusion that the residual current was mostly due to the collision of electrons with gas molecules, and the mean free path of the electrons in these gases was found to agree fairly well with that deduced from the kinetic theory of gases. But in the case of hydrogen, the percentage of residual current was at first found to be NOT directly proportional to the pressure, nor did the

\* Communicated by Prof. O. W. Richardson, F.R.S.

† Phil Mag. vol. xlv. p. 337 (1923).

‡ *Supra*, p. 461.

values at any particular pressure remain constant when larger initial currents were taken. In order to study this effect thoroughly in hydrogen the following investigation was undertaken.

### *Principle of the Method.*

In the present case, the source of electrons was a hot tungsten filament, surrounded by a concentric cylindrical anode. If in a thermionic tube like this, an electric field of potential difference  $V$  is applied between the hot wire and the anode, and a magnetic field  $H$  acts parallel to the wire and so perpendicular to the direction of electric intensity, then, when  $H$  is greater than a certain critical value, the electrons will describe a path round the hot wire in such a way that the maximum distance  $r$  from the axis will be given by

$$H^2 = \frac{8V \log r/a}{e/m \cdot r^2 \cdot \log b/a} + \frac{8V_i}{e/m \cdot r^2} \quad \dots \quad (1)$$

where  $b$ ,  $a$  are the radii of the cylinder and wire respectively, and  $V_i$  the average energy of the electrons at the point of emission.

Taking the values we had in our case, viz,  $b=1.00$  cm.,  $a=.005$  cm., and  $V_i=1.5$  volts,  $V$ , the accelerating potential,  $=4.5$  volts.

$$H^2 = \frac{37.8 \log r/.005}{r^2} + \frac{67.5}{r^2} \quad \dots \quad (2)$$

Thus, if the magnetic field is gradually increased from 0, the current between the wire and the anode will remain constant up to a certain value of  $H$ , then it should fall suddenly to zero as the magnetic field is increased slightly. This will only be possible if all the electrons are coming out with zero or a constant velocity, and *when there is no gas present*. Thus in a perfect vacuum 14.1 units of magnetic field will stop all the current between cathode and anode if electrons are coming out with zero velocity, and 16.0 units if they are coming out with energy corresponding to 1.5 volts—so that if we use a larger magnetic field than this the electrons will have no chance of reaching the anode.

But if, however, there is some gas present, the magnetic field will not stop the current altogether, for a number

of electrons will reach the anode by collision with gas molecules during its passage. Or this residual current might be due to heavy ions formed by electrons combining with gas molecules, and the magnetic field being insufficient, the heavy ions will reach the anode. If the residual current is due to the collisions only, we should be able to get an estimate of the mean free path of an electron in this gas. If, however, the mean free path does not agree with that found otherwise, we can conclude that a certain fraction of the residual current is carried by heavy ions.

### *Description and Arrangement.*

The description of the apparatus used in this experiment has been given in the previous paper (*loc. cit.*) page 342. The only change that has been made in this paper is that instead of the big electromagnet used there, we have a pair of Helmholtz coils which gives the desired magnetic field. The tube is placed half-way along the axis of the coils so that the magnetic field at the centre is uniform and exactly parallel to the length of the hot wire. The filament used here is of tungsten (3 cm. length and .01 cm. diameter), and the cylindrical anode of copper of 4.0 cm. length and 2.0 cm. diameter. They are inserted in the glass tube in such a way that the filament is axial to the anode, and both the ends of the wire are well within the cylinder. The magnetic field is measured by a fluxmeter and checked against the calculated value from the current passing through the coils. The temperature of the filament was found from the Richardson equation

$$i = AT^{\frac{1}{2}}e^{-b/T},$$

and also by measuring the resistance of the filament and comparing with Langmuir's data. Both these methods gave very nearly the same temperature.

Another point of difference in this paper was the use of a less sensitive galvanometer and a micro-ammeter, besides the sensitive one used previously. This was done in order to avoid any mistake that might arise in changing the resistance of the circuit by shunting the sensitive galvanometer for higher values of the initial saturation current. All these galvanometers are arranged in such a way that each could be put into the circuit as desired.

*Experimental Results.*

After joining the thermionic tube with the pump and  $P_2O_5$  bulb, the coils were placed in such a way that the field was parallel to the hot wire. Care was taken to avoid as much as possible any greased taps in the apparatus, so that any vapour arising from them might not interfere with the results. The gas inside the tube was pumped out and the filament was heated very gradually to 2 amps., and all the time the pump was kept in action. In this way all the occluded gases from the filament were taken out. When the pressure inside the apparatus kept constant for three or four hours, the electrode was bombarded by connecting it and the filament with an induction coil, and the evolved gases were pumped out. When there is no more evolution of gas, the tube is in a proper working condition. Now, hydrogen is let in by heating the palladium tube; the whole tube is filled several times with hydrogen and pumped out again before any readings are taken in this gas. All this time, of course, the liquid air is kept in the trap LL, so that mercury, or grease or any other condensable vapour may not come into the apparatus. The spectrum of the gas was also examined, and when only the hydrogen lines were observed, the readings were taken.

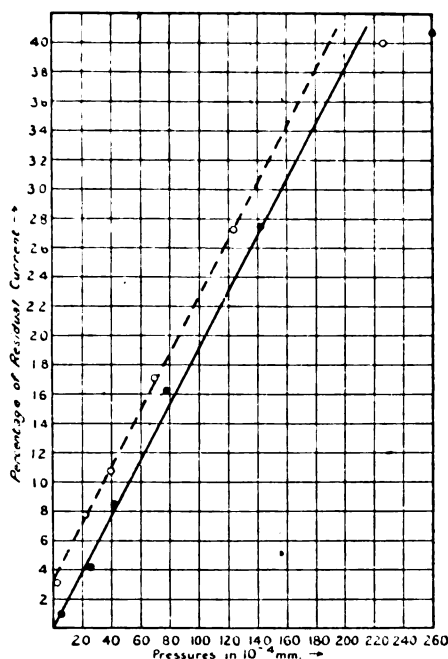
*Effect of Condensable Vapour.*

If no liquid air is kept in L, it is found that there is a residual current in the presence of the magnetic field (170), even at zero pressure, but as soon as liquid air is introduced, this current falls down, though the pressure inside the apparatus is not visibly decreased. This effect of condensable vapour has been noted in the previous paper. It is well shown in fig. 1 where the broken line is drawn through the observational points taken without the liquid-air trap and the full line through those taken with the liquid air in operation. In this case the two lines are parallel showing the effect of the presence of a constant excess pressure, not recorded by the McLeod gauge, of some vapour when the liquid-air trap is not working.

*Effect due to altering the Temperature of the Filament.*

It was noticed during some of these investigations that the percentage of the residual current at a given pressure under the same electric and magnetic fields did not keep

Fig. 1.



constant when the initial saturation current was increased by raising the temperature of the filament. This will be seen from the following:—

TABLE I.

Initial current in scale-divisions.	Percentage of Residual Current at pressures:—				
	$40 \times 10^{-4}$ mm.	$80 \times 10^{-4}$ mm.	$120 \times 10^{-4}$ mm.	$160 \times 10^{-4}$ mm.	$180 \times 10^{-4}$ mm.
3200	4.42	8.84	13.22	17.6	19.8
320	7.8	15.4	23.0	30.2	...

It will be seen from the above that the percentage of the residual current is larger when the saturation current is decreased, *i. e.* when the temperature of the filament is lower, all the other conditions in the experiment remaining the same.



It is of importance to know whether these lower values of the residual current at higher temperatures are due to the wire itself or to some change produced in the gas by the high temperature of the filament. If it were found that the residual current did not go back to its original high value at lower temperatures, after the filament had been once heated to a higher temperature, then we might conclude that the lower percentage of the residual current was caused by some change produced in the filament, such as emission of heavy particles at lower temperatures, which died off as the temperature was raised—this kind of phenomenon is known to exist in new wires. But in the case of hydrogen, it was found invariably that the higher percentage of the residual current repeated itself even after the filament had been heated very strongly. This will be seen from the following results.

TABLE II.

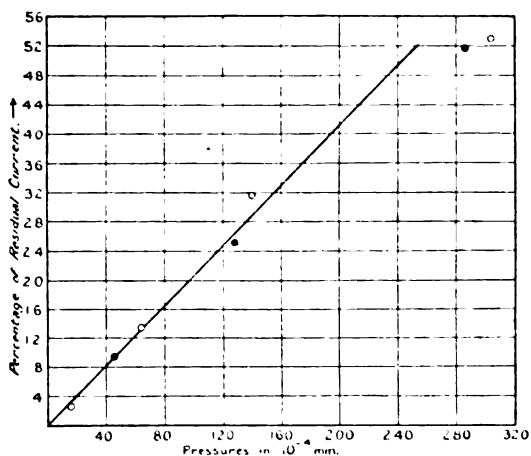
Before.			Temperature increased to give 100-150 times the initial current recorded here.	After.		
Pressure.	Initial current without magnetic field.	Percentage of residual current.		Pressure.	Initial current.	Percentage of residual current.
$294 \times 10^{-4}$	340	53.0		$286 \times 10^{-4}$	340	51.8
140 „	350	31.4		128 „	320	25.0
64 „	350	13.4		48 „	350	9.4
15.5 „	340	2.6		14 „	350	2.59

The readings on the left side of the above table were taken first, after which the filament temperature was raised to give a very high current, and then the readings on the right-hand side taken. These values are plotted in fig. 2, and it will be noticed that both the values of the percentage of the residual current under the action of the fields agree very well.

This shows, at least, that these higher values at lower temperatures are not due to the emission of heavy particles at lower temperatures of the wire, for the heavy emission is stopped completely when the filament is kept at a high temperature for a time. The probable cause of these lower values is that hydrogen is dissociated by the hot tungsten which occurs at about  $1400^{\circ}$  C., *i. e.* at about the same temperature as when the emission from the hot wire begins to be perceptible. So, it is quite possible that when the filament

temperature is raised to give large initial saturation currents, more of the gas is dissociated, and the electrons are colliding with molecular as well as atomic hydrogen. And if the residual current is due to that carried by colliding electrons, then it should depend on the mean free path of the electrons

Fig. 2.



in the gas in the molecular or atomic state; the mean free path being larger when the gas is in the atomic state, we should expect the residual current to be smaller at higher temperatures of the wire. We shall return to the discussion of this later.

#### *Variation of the Residual Current with the Temperature.*

In order to get an idea about the exact amount of residual current at any particular temperature of the wire, the following results were obtained. The higher values of the residual current were recorded by the less sensitive galvanometer  $g$ , and the micro-ammeter. Temperatures were measured by the resistance data and compared with those obtained from the Richardson equation. Hydrogen was let in by heating the palladium tube, and the wire was kept hot; this was repeated several times till the tube was "seasoned" for the experiment. Then, finally, the gas was pumped out to a very low vacuum and fresh hydrogen was introduced before taking the readings. Liquid air was maintained during all these experiments.

TABLE III.

Accelerating potential = 4.5 volts.

(1) Average Temperature of the filament = 1730° K.

Pressure inside the tube.	Initial Current <i>without</i> magnetic field.	Residual Current <i>with</i> magnetic field.	Magnetic field.	Percentage of Residual Current.
$334 \times 10^{-4}$ mm.	120 G	57.5 G	174	47.9
162 ..	125 ..	31.0 ..	170	29.8
67 ..	131 ..	14.0 ..	172	10.7
33 ..	126 ..	6.0 ..	172	4.7

(2) Average Temperature = 1750° K.

$294 \times 10^{-4}$ mm.	340 G	180 G	170	53.0
160 ..	324 ..	100 ..	166	30.8
68 ..	334 ..	44 ..	172	13.1
31 ..	332 ..	17 ..	172	5.1

(3) Average Temperature = 1920° K.

$388 \times 10^{-4}$ mm.	220 g	72 g	168	32.7
330 ..	230 ..	64 ..	172	27.8
158 ..	233 ..	34 ..	170	14.5
67 ..	225 ..	12 ..	172	5.3
29 ..	225 ..	5 ..	170	2.2

(4) Average Temperature = 1970° K.

$380 \times 10^{-4}$ mm.	480 g	123 g	172	25.6
326 ..	485 ..	108 ..	170	23.3
156 ..	490 ..	53 ..	172	10.8
66 ..	478 ..	21 ..	172	4.4
29 ..	485 ..	9.5 ..	170	1.9

(5) Average Temperature = 2015° K.

$372.5 \times 10^{-4}$ mm.	$10.5 \times 10^{-6}$ amp.	218 g	170	18.7
322 ..	10 ..	182 ..	170	16.4
152 ..	10 ..	87 ..	170	7.8
65 ..	10 ..	37 ..	172	3.2
27 ..	10 ..	15 ..	170	1.3

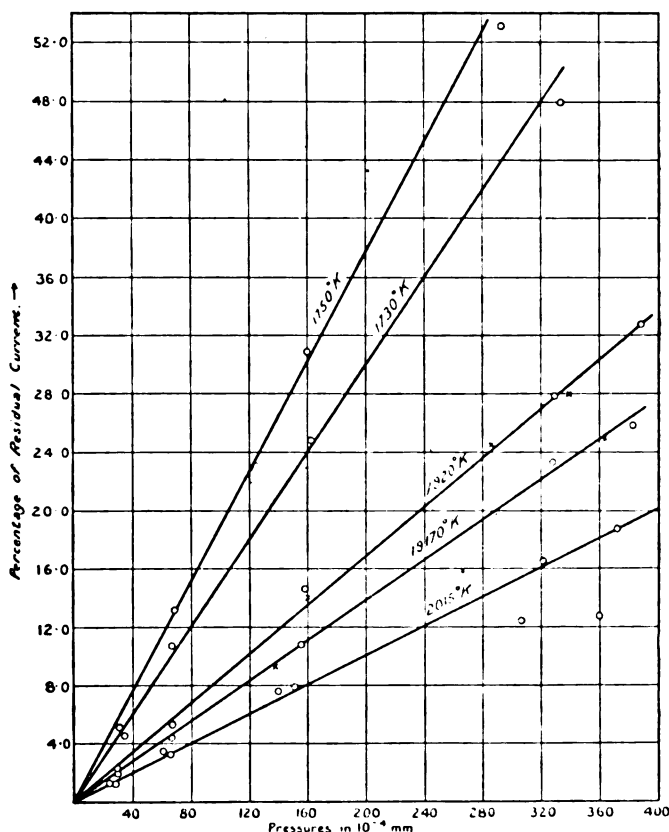
(6) Average Temperature = 2045° K.

$360 \times 10^{-4}$ mm.	$20 \times 10^{-6}$ amp.	280 g	168	12.7
306 ..	20 ..	275 ..	170	12.4
140 ..	21 ..	180 ..	170	7.6
60 ..	20 ..	77 ..	174	3.5
24 ..	20 ..	30 ..	158	1.3

All these points are plotted in fig. 3. It will be seen here that as the temperature of the filament is increased, the

percentage of the residual current decreases gradually to a limiting value. The points marked as **X** are obtained on repeating, after the filament has been raised to a higher temperature. In the above, the lower values of the residual current at temperature  $1730^{\circ}\text{K}$ . are probably due to some

Fig. 3.



error in reading the small deflexion. However, it will be seen here that the percentage of residual current under the action of fields at  $1750^{\circ}\text{K}$ . is 18.9, whereas under the same conditions at temperature  $2015^{\circ}\text{K}$ . it is only 5.1.

### Discussion.

It was shown in a previous paper that such a large percentage of residual current under the magnetic field could be explained on the assumption that the electrons from the

hot wire find their way to the anode after a repeated number of collisions with the gas molecules. It might also be that a certain fraction of this residual current was due to the electrons combining with gas molecules and forming heavy ions. Anyhow, if the first supposition is true, we shall get an approximate value of the mean free path of an electron in this gas, from these data.

The path of an electron inside the thermionic tube, under the action of a magnetic field acting perpendicular to the electric intensity, can be found out from the equation (1), and the length of the path is approximately equal to that of a cardioid, of which the distance between the cusp and the middle point of the curve is equal to the maximum distance  $r$  of the path of the electron from the hot wire.

But the length of the cardioid

$$s = 2 \int_0^\pi a \{ (1 + \cos \theta)^2 + \sin^2 \theta \}^{1/2} d\theta = 2 \times 4a \left[ \sin \frac{\theta}{2} \right]_0^\pi = 8 \cdot a \\ = 4 \times \text{maximum distance } r.$$

In our case, the magnetic field was about 170, and the applied potential between the filament and the anode was 4.5 volts. Besides we have to take into consideration the potential drop of 1 volt per cm. along the filament, due to which we shall have a total drop of 3 volts (because the filament is of length 3 cm.) Thus at the middle point of the filament we shall have a drop of 1.5 volts, which will thus give a total accelerating potential of  $4.5 + 1.5 = 6.0$  volts. Taking this latter value of  $V$ , we get from equation (2)

$$r = .085 \text{ cm.}$$

$$\therefore \text{length of the path } (s) = 4 \times .085 = .34 \text{ cm.}$$

Now, the fraction which collides in path  $x$  is  $e^{-x/\lambda} \frac{dx}{\lambda}$ , so that the fraction which collides in the total path  $s$

$$\xi = \int_0^s e^{-x/\lambda} \frac{dx}{\lambda} \\ = 1 - e^{-s/\lambda},$$

$$\therefore \lambda = - \frac{s}{\log_e(1 - \xi)}.$$

In the above equation, we know  $s$  and  $\xi$ , and so we can find  $\lambda$ .

Thus, corresponding to the topmost part of the curve  $\xi_1 = .189$  we get the mean free path of the electron at  $10^{-2}$  mm. pressure

$$\lambda_1 = -\frac{s}{\log_e(1-\xi_1)} = -\frac{.34}{\log_e .811} = 1.63 \text{ cm.,}$$

i. e., the mean free path  $\lambda_1$  at 760 mm. and  $0^\circ \text{C.} = 2.15 \times 10^{-5}$  cm. Similarly, corresponding to the lowest curve, the mean free path at  $10^{-2}$  mm.

$$\begin{aligned} \lambda_2 &= -\frac{s}{\log_e(1-\xi_2)} \\ &= \frac{.34}{\log .949} = 6.54 \text{ cm., where } \xi_2 = .051, \end{aligned}$$

i. e., m.f.p. at 760 mm. and  $0^\circ \text{C.}$  is  $8.5 \times 10^{-5}$  cm.

Thus the mean free path of an electron, obtained by this method, in hydrogen increases from  $2.15 \times 10^{-5}$  at about  $1740^\circ \text{K}$  to  $8.5 \times 10^{-5}$  cm., at  $2015^\circ \text{K}$ . Now, the mean free path of an electron in a gas in the atomic state is also about four times that in the molecular state (assuming the diameter of the molecule to be twice the diameter of the atom). What happens, therefore, in our case, is that the electrons are colliding with gas molecules when the temperature of the filament is low and with atoms when the temperature is high—the molecular hydrogen being dissociated into the atomic state by the hot filament. At temperatures between these two limits, the electrons are colliding with molecules as well as atoms.

The mean free paths obtained by this method as compared with those obtained in the kinetic theory on the assumption of the diameters of electrons and molecules and atoms, are

	Kinetic Theory.	This Method.
For molecules	$6.3 \times 10^{-5}$ cm. at 760 mm.	$2.15 \times 10^{-5}$ cm. at 760 mm.
„ atoms ...	25.2 „ „	8.5 „ „

The smaller values of the m.f.p. in hydrogen might be due to the fact that in our calculation above we have taken the whole of the residual current to be due to the electrons colliding with gas molecules and reaching the anode as electrons. If, however, a certain fraction of this residual

current be due to the heavy ions, then  $\xi$  will be smaller and  $\lambda$  will be bigger. Sir J. J. Thomson has found some evidence of the existence of heavy ions in hydrogen, so that it is quite possible that the whole of the residual current is not carried by electrons only. Besides, we have assumed that the temperature of the gas surrounding the hot wire is zero, but it actually varies from point to point along the radius of the anode.

*Summary.*

(1) It has been shown in this paper that the percentage of the residual current in hydrogen depends to a large extent on the temperature of the hot filament.

(2) The residual current comes back to its value at any particular temperature, even after the filament has been heated to give 100-150 times its initial saturation value.

(3) The residual current under the action of the crossed fields is proportional to the pressure up to at least  $2 \times 10^{-2}$  mm.

(4) The current is probably carried mainly by electrons colliding with gas molecules at the lower temperatures, and with dissociated atoms at the higher temperatures.

(5) The mean free paths of the electron in hydrogen in the molecular as well as in the atomic state have been estimated. These values are lower than those given by the kinetic theory of gases. No accurate determination of the m.f.p. is possible, however, until the fraction of the residual current carried by heavy ions is known.

In conclusion I must thank the Radio-Research Board for financial assistance in the carrying out of this investigation. I wish, also, to express my gratitude to Prof. Richardson, F.R.S., for his suggestions and advice during the course of the work.

Wheatstone Laboratory,  
King's College, London.

LX. *Unit Curves of a Photographic Lens.* By ALICE EVERETT, M.A. (*From the National Physical Laboratory.*) \*

A PREVIOUS note (Phil. Mag. vol. xlv. p. 450, 1923) described the unit curves of a solid sphere, which regarded as a lens is an uncorrected system. The figures accompanying the present note show unit curves for an axial section of a corrected photographic lens, a Tessar, for three different positions of an infinitely distant source.

Tessar (1907).  $f_D=100$ . Aperture ratio  $=f/4.5$ .

	Radius.	Thickness.	
1 .....	+ 26.3	3.7	1.61342
2 .....	$\infty$	4.0	1
3 .....	- 58.1	1.7	1.57391
4 .....	+ 23.9	5.3	1
5 .....	- 146.7	1.7	1.53
6 .....	+ 22.3	4.6	1.61451
7 .....	- 36.3		

To obtain these curves, three sets of parallel rays at inclinations  $0^\circ$ ,  $5^\circ$ , and  $20^\circ$  to the axis, and apertures 0,  $\frac{1}{3}$ ,  $\frac{2}{3}$ , full, were traced through the system in an axial plane, and on each ray the positions of the two pairs of unit points, primary and secondary, were found by putting the magnification equal to unity in Mr. T. Smith's formulæ connecting focal distance with magnification (Proc. Phys. Soc. vol. xxvii. p. 508 (1915) and vol. xxx. p. 232 (1918)). These positions were then transformed to rectangular coordinates, and plotted, taking the optic axis as axis of  $x$ , the first vertex of the lens as origin for the object space, and the last vertex as origin for the image space.

The incident ray is defined by its inclination  $\psi$  to the optic axis, and aperture, the aperture for the present purpose being measured by the length of the perpendicular on the ray from the vertex of the lens, and called "full" when this length is equal to the semi-diameter of the front lens.

The object and image unit curves are drawn separately to avoid overlapping. The paraxial unit points of the Tessar lie near the centre of the lens, only 1.0525 apart for a focal length 100, the first point being 8.7961 behind the first surface.

The secondary unit curves are shown in fig. 1, and the primary unit curves directly underneath them in fig. 2. Inspection shows that the following conclusions apply to both.

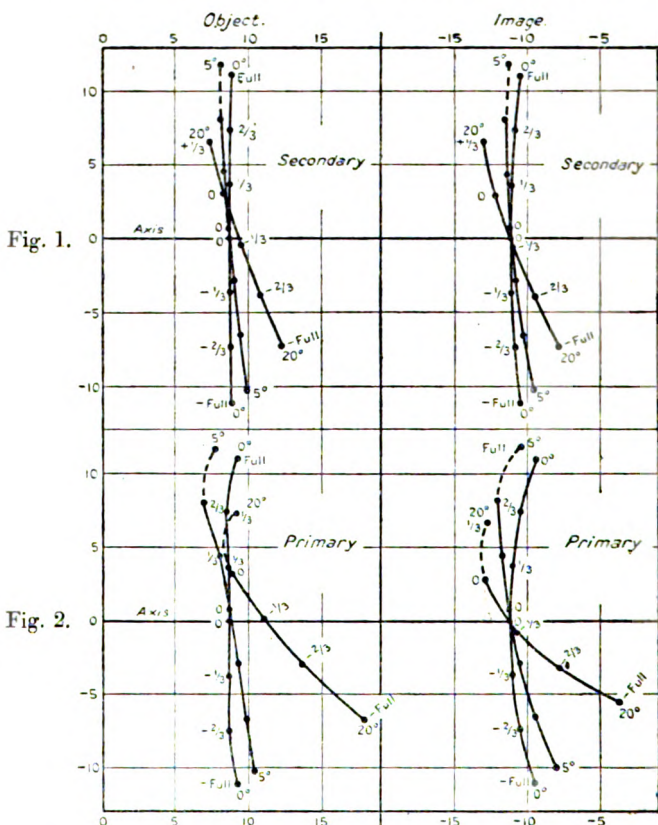
\* Communicated by the Author.



*Conclusions.*

(1) The position of the unit curves changes with that of the source, *i. e.* with the inclination of the parallel pencil of chief rays.

(2) The curvature changes with the position of the source.



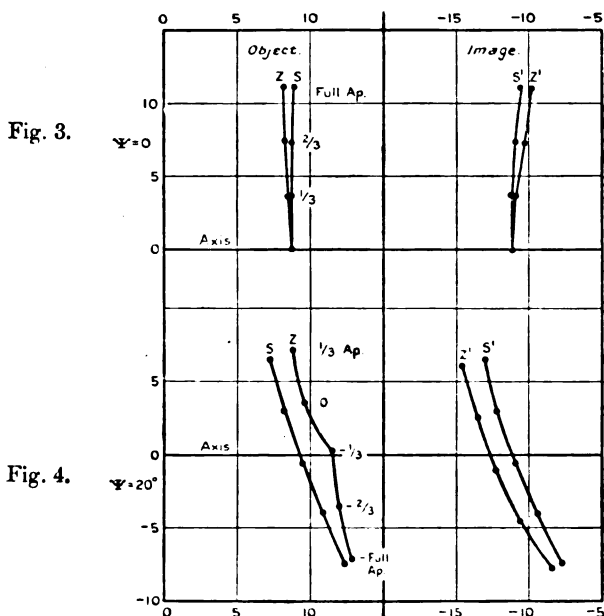
(3) The curvature changes also with the aperture or incident height; the curves are not circular, nor plane. Hence the object curves cannot coincide with the incident wave-front, which is plane.

(4) The unit curve in the image space, like the wave-front, is more convex to the source than the curve in the object space.

The primary unit curves exhibit greater variations in curvature than the secondary unit curves; moreover, while

the secondary curves are only slightly inclined to the wave-fronts, the primary curves for the higher inclinations show a very decided slant. The secondary curves are practically all convex to the source. The primary object curves are concave in parts, but on the other hand the primary image curves are more convex than the secondary image curves.

Each of the curves drawn is only a partial image (if image it can be called at all) of its conjugate. The image of each unit curve is astigmatic. Fig. 3 for  $\psi = 0^\circ$ , and fig. 4 for



$\psi = 20^\circ$  may serve to give an idea of the amount of astigmatism.  $S, S'$  are secondary unit curves, and the curves  $S', Z'$  on the right are the secondary and primary images of  $S$  on the left.  $Z'$ , of course, is not the same as the corresponding primary unit image curve. The curves  $S, Z$  on the left would be the secondary and primary images of  $S'$  for light travelling backwards.

Primary unit curves (not shown here) on the assumption of unit magnification perpendicular to the optic axis, instead of to the ray, have a still more marked slant than those drawn, and otherwise show greater departure from the secondary forms.

Unit curves of a Cooke lens (1894) have also been plotted and show much resemblance to those given here.

LXI. *Notices respecting New Books.*

*The Air and its Ways. The Rede Lecture (1921) in the University of Cambridge, with other contributions to Meteorology for Schools and Colleges.* By Sir NAPIER SHAW, Sc.D., F.R.S. (Pp. xx+237, with 28 plates and 100 figures.) (Cambridge: at the University Press, 1923. Price 30s. net.)

THIS volume contains a number of articles, papers, addresses, and miscellaneous contributions to meteorology by Sir Napier Shaw. They are concerned mainly with the physical explanation of the atmospheric circulation, though a few at the end are concerned with the application of meteorology to agriculture. The subjects dealt with are therefore of very general interest; and as the volume is written in the author's characteristic lucid style, it should offer a wide appeal not only to students and teachers, but also to the general reader. It is an easy matter to criticize the Meteorological Office on account of inaccuracy of weather forecasts, but an intelligent perusal of this book will bring home to the critic the complex processes concerned in the phenomena of atmospheric circulation. The volume contains a series of 24 plates, designed to represent the normal distribution of the meteorological elements over the globe. There are many figures in addition which help to make it easy to follow the arguments.

There are many readers who would be deterred from reading a text-book on meteorology to whom this series of essays which ramble from one subject to another, but which all illustrate the general physical principles at work, will appeal. Sir Napier Shaw is to be congratulated on a volume which would serve to stimulate interest in a subject which closely concerns us all.

*The Analysis of Spectra.* By W. M. HICKS. Pp. vi+326. Cambridge University Press. Price 35s.

PROFESSOR HICKS has seen the subject to which he has devoted so much time and energy grow from being the province of the few to one of the most widely studied branches of physics. Having had his work crowned by the award, in 1921, of the Adams Prize for an essay dealing with the Analysis of Spectra, he has now extended that essay into a treatise on the subject which is sure of the respectful attention of all spectroscopists.

The treatise has as its chief object the systematic presentation of the knowledge of the structure of line spectra which has been won by the study of the experimental data, without reference to or guidance from any special theory of the origin of spectra. Little use, for instance, is made of the quantum theory of spectra, not because any arguments are urged against it, but because the author's unlimited capacity for computation has enabled him to

reach empirical results whose validity he wishes to be judged simply by comparing them with the available measurements. This neglect of Bohr's theories sometimes leads to discussion which will appear pointless to the disciples of the quantum school; but this is inevitable where, to quote the author's words, "the data are studied in a purely objective manner, without any preconceived opinions based on theories as to the cause or manner of production."

Chapter I., which discusses standards, and the character and degree of accuracy of data, and Chapter V., on the effect of physical conditions, are altogether excellent. The latter contains a detailed discussion of the chief experimental results on the Zeeman effect, and emphasizes its value as an aid in the analysis of spectra: the Stark Effect and the investigations of Stark and his school on the Doppler Effect observable with positive rays are also discussed, and some space is devoted to radiation and ionization potentials, but here the neglect of recent theory is very noticeable. In Chapter II. the author deals with the types of series and their representation by formulæ, and with those regularities which have been discovered in spectra where no series have been identified, and he follows this by discussing in detail the systems of series of the elements in each chemical group in turn. The monatomic gases, with the exception of helium (considered earlier), have a chapter to themselves towards the end of the book.

The data for the elements and their allocation into series, combinations, and groups are given in tabular form in the Appendix under a single heading, Table III. This, however, is actually a long set of tables extending over 75 pages. For the representation of the series the Hicks formula is, naturally, employed, and the values of the constants for the various series in Table III. are collected in Tables IV. and V. of the Appendix. If Professor Fowler's 'Report' had not appeared at about the same time as Professor Hicks's book, these tables would be of unique value.

Much of the 'Treatise' is based on the author's own extensive contributions to the subject, so that naturally considerable space is devoted to the special conceptions which he has introduced—the *oun*, displacements, links, and summation series. The necessity or utility of these conceptions, singly or collectively, is, it is true, contested by many spectroscopists. Discussion of such a debatable point is obviously out of place in a short notice like the present, for definite assertions as to the existence of the regularities expressed by these terms can clearly be made with safety only after an independent and exhaustive analysis by a spectroscopist with great experience in the handling of the experimental data. As regards the summation series, we will only venture to remark that, although many observed lines have been allocated to these series the tables show frequent irregularities of intensity and character, as well as some instances of the inclusion of arc, spark, and displaced lines in one and the same summation series.

Amongst such a mass of figures it is obviously unreasonable to expect a complete absence of errors. One mistake appears to be recurrent in the tables of the P series of the alkali metals, and in the S series of Zn, Al, and Tl. The values of  $m$  in the P tables of Na, K, Rb, and Cs must be reduced by unity throughout if the constants tabulated on page 316 are to apply. The values of  $m$  in the P terms in the combination tables of Na and Cs are in accord with the P formulæ constants, but not with the values of  $m$  in the P tables of these two elements. On the other hand, the values of  $m$  in the P terms in the combination tables of K and Rb agree with those in the P tables, but do not correspond with the P formulæ constants. This applies also to Na combination 13. There are errors of a similar nature in the Zn combinations and the sharp doublets of Al and Tl.

Readers acquainted with the abbreviated notation introduced by Paschen will perhaps experience a little inconvenience on first reading the present treatise. Professor Hicks represents the  $m$ th "term" or "sequent" by  $P(m)$ ,  $s(m)$ ,  $d(m)$ ,  $f(m)$  instead of by  $mP$ ,  $mS$ ,  $mD$ ,  $mF$ . Again, the notation for doublets and triplets differs from that generally used. No doubt arguments can be advanced in favour of the retention of Rydberg's "index numbers," but it is a pity that some agreement cannot be reached among spectroscopists as regards the notation to be used. The unfamiliar appearance of the symbols to those accustomed to the notation of Professor Fowler and his school may prevent many from making the best use of Professor Hicks's extremely painstaking and praiseworthy treatise.

*Collected Scientific Papers of John Aitken.* Edited by CARGILL G. KNOTT. Pp. xxi+591. Cambridge University Press. 30s.

DR. AITKEN'S name is best known to physicists through his experiments on the condensation of water on dust particles, which follows on the slight supersaturation produced by a small expansion of moist air. The behaviour of dust particles as nuclei of condensation was actually observed by Coulier in 1875, before Aitken started his researches; but Aitken did not know of this, and built up his large and valuable body of research in this direction on original observations made by himself. His work on the part played by atmospheric dust in meteorological phenomena, his elegant dust counters, and the application of his methods to electronic measurements are too well known to need emphasis. The most important part of his other work is that dealing with the formation of dew, in the course of which he made the interesting discovery that the "dew drops" on the leaves of plants are exuded by the plant itself. He was keenly interested in all branches of meteorology, and wrote on the problem of the genesis and maintenance of cyclones, on hoar frost, ground ice, and other kindred subjects. The volume before us contains not all his

papers, but a full selection made by Dr. Cargill, who has prefixed to the collection a short account of the author's life. All the important papers are printed in full, and the volume, admirably produced by the Cambridge University Press, forms a fitting memorial of the modest and gifted investigator whose life-work it represents.

*The Theory of Spectra and Atomic Constitution.* By NIELS BOHR.  
Pp. x+126. Cambridge University Press. Price 7s. 6d.

PROFESSOR BOHR's work is too well known to all readers of the *Philosophical Magazine* for this book to require commendation. It consists of three essays in which essential features of his theory of atomic structure are developed in simple language, with but little resort to mathematical symbols. The first essay dates from the end of 1913, and gives an account of his pioneer work on the spectrum of hydrogen, which first established the quantum theory of spectra: it is translated from a Danish address. The second essay, translated from the *Zeitschrift für Physik*, is based on an address delivered in 1920, in which consideration is devoted to the application of the theory to certain general features of series spectra, and, in the relatively simple case of hydrogen, to the Zeeman and Stark Effects and the fine structure of spectral lines. The famous Correspondence Principle receives a general explanation here. The third essay, based on a Danish address given towards the end of 1921, deals more particularly with the general theory of the structure of the atom, and the variation of atomic properties expressed in the periodic table. The essential feature of Bohr's newest developments, i. e. the variation of strength of binding of the electron last added as we proceed from lighter to heavier atoms, which leads in the long periods to the completion of inner groups after outer groups of electrons have been begun, is here expounded, and its important consequences emphasized. The nature of the evidence that can be derived from a study of the spectra is, of course, clearly indicated.

There is a certain amount of inevitable overlapping in the three essays, but this is rather to be welcomed than deplored, as it enables the reader to trace the development of the theory by the author from its inception to the start of the latest phase. The book is assured of the warm welcome it deserves as an authentic exposition of the work of one of the most original minds now active in the domain of physics.

*A Theory of Natural Philosophy.* By ROGER JOSEPH BOSCOVICH, S.J. Pp. xix+470. Open Court Publishing Company.  
Price £3 3s.

THIS handsome folio volume embodies the chief work of Father Boscovich, being a reprint of the *Theoria Philosophiæ Naturalis*, first published in 1758. The Latin text, now printed for the

sixth time, is given on the left-hand page, the opposite page being devoted to an English version by Mr. J. M. Child. As far as we know, this is the first time that the work has been translated into a modern tongue. It is prefaced by a short life of the author, written by Dr. Branislav Petroniević, and an explanatory introduction by the translator.

Boscovich's 'Natural Philosophy' is a work of considerable importance in the history of physical theory, and his atomic hypotheses—if they may be so called—are of particular interest to-day. He considers all matter to be made up of discrete points, "points that are perfectly simple, indivisible, of no extent and separated from one another," acting upon one another with a universal, if somewhat complicated, law of force. At very small distances two of Boscovich's points repel one another, and for very close approach the repulsive force tends to become infinite, so that two points can never be brought into coincidence. As the points are separated, the repulsion becomes an attraction, and as the separation is further increased, the force oscillates several times between repulsion and attraction, until finally, when the distance becomes large, the Newtonian law of attraction is approached more and more closely. The oscillations are invoked to explain evaporation, chemical generation of gases, including explosions, and are further utilized in the exposition of the corpuscular theory of light, of which Boscovich was an ardent supporter. The simple hypothesis of one reversal point between repulsion and attraction suffices to explain many of the properties of matter, such as cohesion and elasticity. The courageous attempt to explain all physical laws in terms of discrete centres of force entitles Boscovich to rank as one of the founders of our present atomic theories. Much of the book is very modern in spirit. The centres of force, all of one kind and governed by the same laws, remind us inevitably of electrons: the insistence on the penetrability of matter, illustrated by the analogy of an iron ball, moving with great velocity, making its way freely through a group of magnets, is an astonishing anticipation of Rutherford's work on the  $\alpha$  particle. Too much stress must not, of course, be laid upon such general anticipations, but the average reader who takes upon this book will probably be astonished by the power and directness of Boscovich's attack on the great problems of physics, and the scope of his method.

Although often called an Italian, notably in the biography in the *Encyclopædia Britannica*, Boscovich was of Slav descent, and prided himself on it. He was born at Ragusa, and on his father's side the family was of purely Serbian origin. The expenses of producing the present volume have been largely borne by the Government of the kingdom of Serbs, Croats, and Slovenes, an enlightened act in the interests of Slav science. We do not know why so large a format (15 × 11 inches, an awkward size for most bookshelves) has been chosen, especially as the original Venetian edition of 1763,

from which the text is taken, is a quarto of ordinary size. It is also strange that the original had to be borrowed from the Cambridge University library, which apparently involved some inconvenience, since the book is by no means very scarce, and can occasionally be purchased for less than the cost of the present edition, which will, however, be invaluable to those, and they are many, whose Latin is uncertain.

## LXII. *Proceedings of Learned Societies.*

### GEOLOGICAL SOCIETY.

[Continued from p. 224.]

March 14th, 1923.--Prof. A. C. Seward, Sc.D., F.R.S.,  
President, in the Chair

**THE** following communications were read:—

1. 'The Geology of the Schists of the Schichallion District of Perthshire.' By Ernest Masson Anderson, M.A., B.Sc., F.R.S.E., F.G.S.

An examination of the area between Carn Mairg and Schichallion reveals the presence of the following succession:—Graphite-Schist: Pebbly Quartzite: Mica-Schist: Non-pebbly Quartzite: Schichallion Boulder-Bed. The Graphite-Schist is undoubtedly that which borders the Ben Lawers (Caenlochan or Calc-Sericite) Schist, and its position can therefore be fixed with regard to the undisputed part of the Perthshire Dalradian succession. It is inferred (*a*) that the Boulder-Bed is on the opposite side of the Quartzite from the Graphite-Schist, and the sequence which extends from the Ben Lawers Schist to the Ben Ledi Grits; and (*b*) that the Quartzite itself is heterogeneous, and must be regarded as a composite group.

Following the Boulder-Bed, and thus on the same side of the Quartzite, are a white limestone, a banded series of siliceous and micaceous rocks, a grey carbonaceous limestone, and a slightly carbonaceous mica-schist, which may be named the 'Grey Schist'. On approach to the white limestone the Boulder-Bed becomes highly calcareous. It seems likely that this conglomerate is a tillite, and the evidence suggests that it has been partly formed from the material of the limestone. If so, the latter is the older. There may thus be a chronological sequence, of which the oldest visible member is the Grey Schist, extending upwards to the Ben Ledi Grits in an adjoining part of Perthshire.



In the northern part of the Schichallion district the Dalradian Series is bordered by the Struan Flags. The latter probably underlie the former, while the boundary is a line of discordance. There is some evidence for the conclusion that the junction is not an unconformity, but either a normal fault which has been affected by strong horizontal movement, or else a folded thrust.

2. 'The Petrology of the Arnage District in Aberdeenshire: a Study of Assimilation.' By Herbert Harold Read, M.Sc., A.R.C.Sc., F.G.S.

This paper deals with the modification of magmas by the incorporation of material of sedimentary origin, a process to which the name contamination is given. In the Arnage mass in Aberdeenshire—one of the outcrops of what is probably an extensive gabbro-sheet—the sediments concerned in contamination are: (*a*) andalusite-schists and pebbly grits of the Fyvie Series; and (*b*) biotite-schists and subordinate hornblende-schists of the Ellon Series.

The contaminated rocks occur as a roof-zone, some hundreds of feet thick, overlying a sheet of norite rich in magnesia. The contaminated rocks are of four types:—

(1) Gabbro Type, occurring as small patches kneaded in among the other types.

(2) Arnage Type, consisting of various associations of quartz, cordierite, oligoclase-andesine, alkali-felspar, and biotite, with garnet, spinel, and tourmaline; the contaminators are argillaceous schists.

(3) Kinharraichie Type, a dioritic type produced by the contamination of the initial magma with hornblende-schist.

(4) Ardlethen Type, a granitic type transitional from the other types.

The first three types hold xenoliths, while the fourth is practically free from them. The xenoliths are rich in cordierite, spinel, sillimanite, and basic felspar, with some hypersthene.

On the assumption, for which there is some evidence, that the initial magma was normal gabbro, it is shown that the contamination-process depends on reciprocal reaction between initial magma and xenoliths, whereby the magma loses magnesia and lime and becomes richer in alumina and alkalies, the final results of the reciprocal reaction being the granitic Ardlethen type of contaminated rock and certain xenoliths extremely rich in magnesia and lime.

The operation of gravitative cleansing is examined: the modified xenoliths sink in the acidified magma of the contaminated zone; and they pass into the underlying sheet of initial gabbro, which becomes enriched in magnesia and lime, with the formation of the norite now seen beneath the contaminated zone.

The relations of the contamination-process to the assimilation hypothesis of magmatic differentiation are briefly discussed. Certain criticisms of the assimilation hypothesis can be met by the

principle of reciprocal reaction. The chemical variation in the contamination-process is exactly the same as that in igneous rocks as a whole, and it is considered that reciprocal reaction may play a part in magmatic differentiation, especially in the great gabbro-sheets.

March 28th, 1923.—Dr. Herbert H. Thomas, M.A.,  
Vice-President, in the Chair.

The following communication was read :—

‘Further Researches on the Succession and Metamorphism in the Mona Complex.’ By Edward Greenly, D.Sc., F.G.S.

Since the publication of the Anglesey Geological Survey map and memoir, various aspects of this complex have been further investigated, and the following are some of the results.

The age of the Complex.—Fragments lately obtained from the Volcanic Series of Bangor show that the metamorphism of the Complex is older than that series.

The Gwna Beds.—Five new analyses of the quartzite are given; fresh evidence is adduced that the basic schists of the Eastern Aethwy Region are derived from the spilitic lavas; and two more occurrences of spilitic tuffs are described, the relations of which to adjacent jaspers and limestones indicate that the latter are not metasomatic products, but original sedimentary formations. A singular effect of anamorphism in its earliest stages is that quartz-epiclasts have been corroded and invaded by the carbonates of a calcareous grit.

The Fydllyn Beds.—A partial analysis is given of one of the rhyolitic tuffs. Fydllyn Beds have lately been identified at Mynachdy and two other places in the northern region. Their identification at Mynachdy throws great light on the succession, and, by indicating inversion, on the tectonics also.

The Penmynydd Zone.—Titaniferous varieties of the Bodwrog marble furnish evidence as to the conditions of development, under dynamic metamorphism, of rutile and of sphene. A small inlier of the Zone, lately discovered, with unusually clear passages from the Gwna mélange, throws light on the origin of the Penmynydd-Zone mica-schist and anamorphic processes.

The Ancient Floor.—More fragments of ancient crystalline schists have been found, one of them being in the Fydllyn Beds, a lower horizon than any that had hitherto yielded any such fragments.

The age of the Gneisses.—The discovery of the Fydllyn Beds at Mynachdy, of late dynamo-anamorphism in the adjacent

gneisses, and of a gneissose fragment in the Fydyln Beds, confirms the view that the gneissic structures are older than the deposition of the Bedded Succession.

The origin of the basic gneisses.—Banding is shown to have resulted from deformation of a differentiated basic magma at an advanced stage of consolidation. Three generations of pegmatite are distinguished, the earliest of which is subsequent to the consolidation of the banded gneiss. Yet foliated hornblende has developed in the gneiss in connexion with their segregation.

The relations of the basic and acid gneisses.—Granitoid banding has been found to be subsequent to granitoid permeation, so also has the appearance of the basic magma from which the hornblende gneisses were developed. Thus, the micaeous gneisses must be regarded as the oldest known member of the Gneissoid Complex.

### LXIII. *Intelligence and Miscellaneous Articles.*

#### THE THEORY OF THE ABNORMAL CATHODE FALL.

*To the Editors of the Philosophical Magazine.*

GENTLEMEN,—

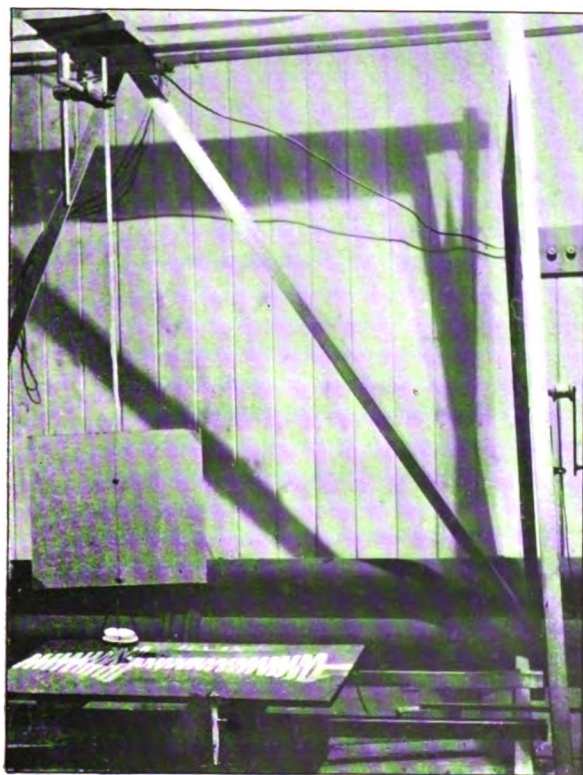
WE hasten to assure Dr. Aston that we did not overlook any part of his important work. We did not mention his theory because, as he admits, it differs from ours in the only feature to which we attribute much importance. The whole object of our paper was to suggest that a theory of the abnormal fall is not impossible, in which it is supposed, in accordance with several lines of recent work, that the positive ions reach the cathode with nearly the full energy corresponding to the fall.

For the rest, we fully admit and indeed drew attention to the discrepancies which he notes. But we still believe that it may prove possible to remove these discrepancies when further knowledge is available concerning those factors which we mentioned explicitly as excluded from our preliminary theory.

Yours faithfully,

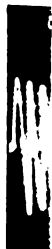
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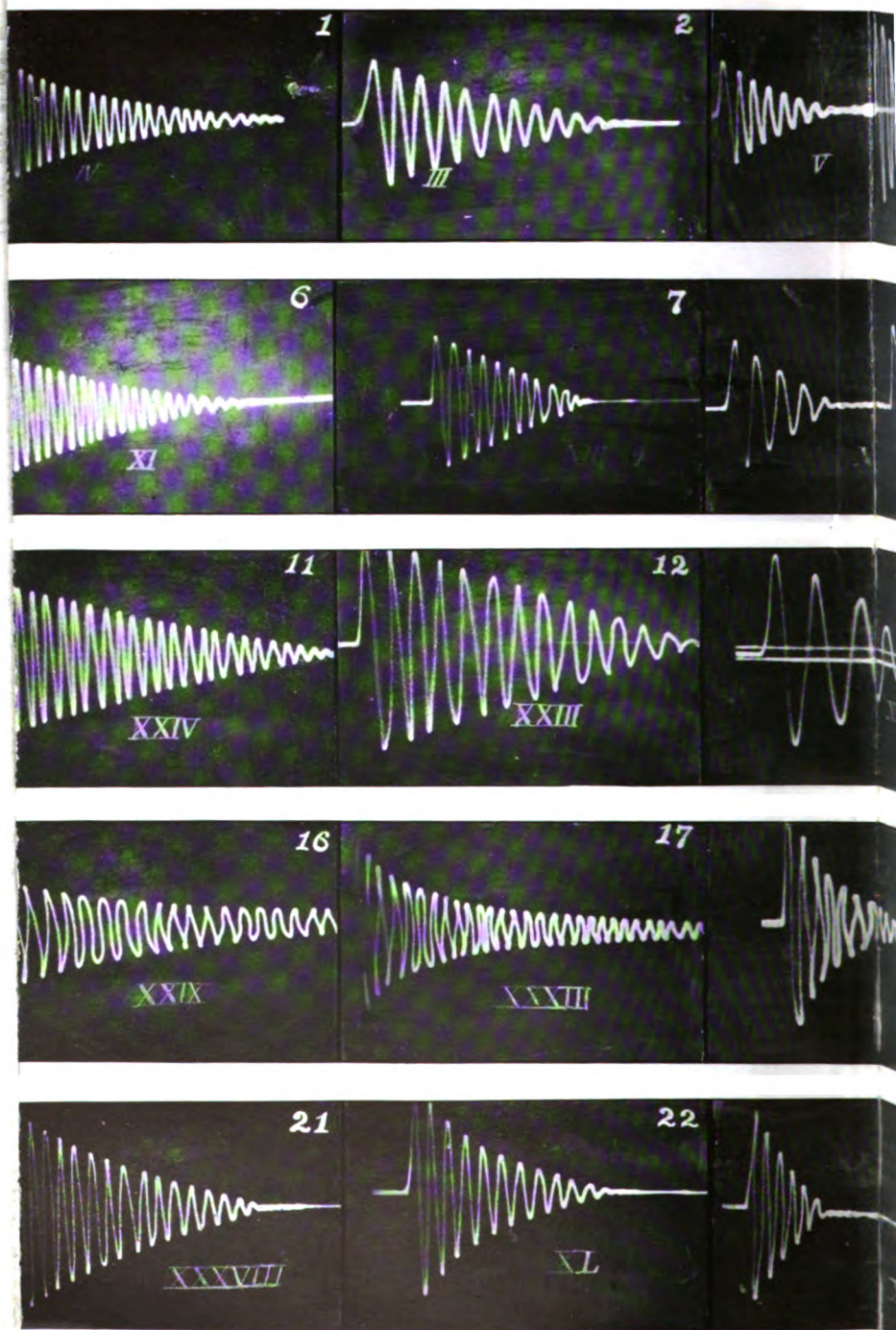
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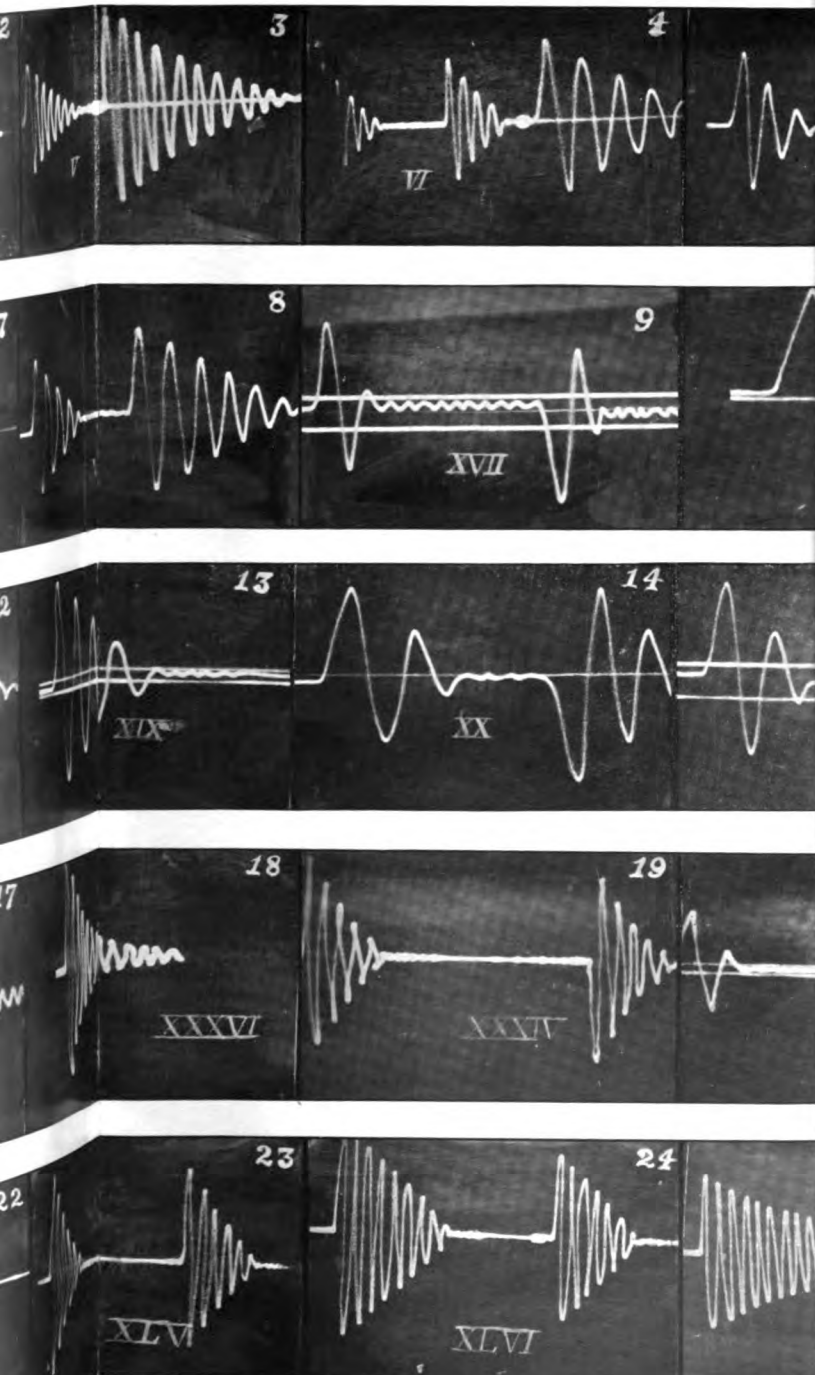


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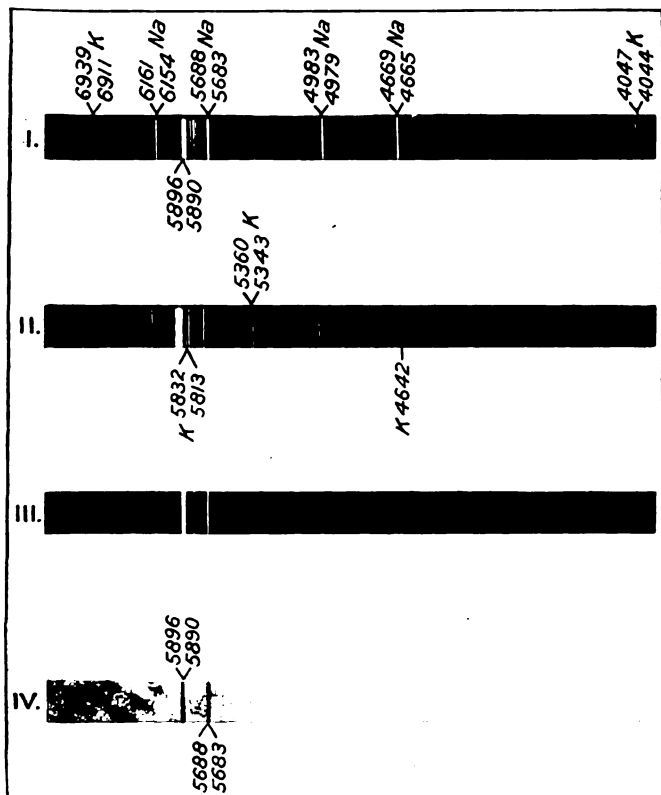
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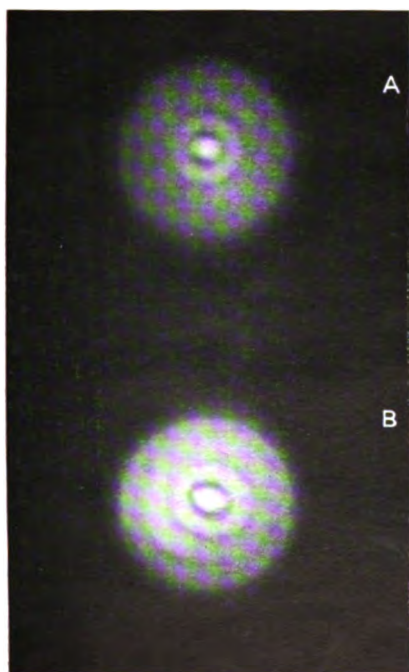
I. Spectrum from alloy vapour lamp.

II. Radiation from lamp passed through feebly luminous sodium vapour.

III. Radiation from lamp passed through feebly luminous sodium and potassium vapours.

IV. White light passed through feebly luminous sodium vapour.







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LXIV. *The Constitution of the Upper Strata of the Atmosphere.* By L. VEGARD, D.Sc., Professor of Physics at the University of Christiania\*.

[Plate X.]

*Auroral Spectra at different Altitudes.*

§ 1. **I**N a communication recently published † I gave the results of investigations on the auroral spectrum: carried out during last winter. Since I wrote this paper I have, during a stay at Tromsø from the end of February to the end of March, been able to carry out further observations on the auroral spectrum, and above all I have succeeded in taking spectrograms corresponding to various altitudes. At the same time I have continued investigations on the distribution of gas density in an electrically-charged atmospheric layer.

These investigations have confirmed the view already announced in my first paper with regard to the substances present in the higher strata of the atmosphere and the origin of the green auroral line, but with regard to the physical state of these strata they have led to a modification of the view announced in my first paper.

In this supplementary communication I am going to give a short account of the results of these investigations.

In the first paper we saw that most of the lines appearing in the auroral spectrum are due to nitrogen, but the strongest

\* Communicated by the Author.

† Phil. Mag. July 1923, p. 193.



of all lines (the green line) and three faint lines in the blue and the ultra-violet could not be found among the lines of nitrogen observed in laboratory experiments and given in the tables of the spectral lines.

Nor can they be found among the known lines of hydrogen and helium. Already this result suggests that also the green line and the other three not identified lines are due to nitrogen.

The spectral lines given in my first paper were photographed by directing the instrument towards the strongest parts of the auroræ, and the spectra thus obtained will be mainly determined by the light emitted in a height interval near the bottom edge between 100 and 120 km. say. In this interval nitrogen is found to be a predominant component, and in this interval also the green line appears with a very great intensity.

If the green line is emitted from some gas which is different from nitrogen and which has not entered into any kind of combination with this element we should expect that the intensity of the green line relative to that of the nitrogen bands would change rapidly as we pass upwards from the bottom edge of an auroral streamer.

By means of a simple spectroscope I have examined the light emitted from various parts on very long auroral rays, and it appears that the green line is emitted to the very extreme upper limit of rays reaching altitudes of several hundred kilometres. The nitrogen bands have a very small effect on the eye and a very strong aurora is required to make them visible in a spectroscope, and in the case of long ray streamers the N-bands are usually not noticeable. We are thus under the necessity of using a photographic method for the solution of our problem.

For this purpose we want a spectrograph of the very greatest light power, but as we are only studying intensity variations we need no great dispersion. Already in the first paper I have mentioned that a small spectrograph of great light power was constructed for studying the possible variations of the auroral spectrum (spectrograph nr. III.).

Before I went to Tromsø this winter I had a second spectrograph of the same type made, and in this way I was able to work with two spectrographs simultaneously. It will be of interest in this connexion to give a short description of these instruments.

In the construction of the instrument I made use of the fact that the light power of a spectrograph does not depend on the light power of the collimator lens, provided that the

camera lens has a great light power. The smaller light power of the collimator lens is compensated by using a wide slit.

The construction of spectrographs on this principle has the following advantages :—

- (1) The effective cone of the instrument can be filled with light from a source of light which has fairly small angular dimensions seen from the slit.
- (2) A lens of small light power is cheaper and easier to make.
- (3) As the picture of the slit is much reduced the slit need not be so exactly made to give equally good lines on the picture.

The collimator lens had a diameter of 3 cm. and a focal distance of 18 cm. The camera lens had an effective opening of 2.5 cm. and a 5 cm. focal distance, and thus the light power was 1 : 2. Rutherford prisms were used in both spectrographs.

On the collimator could be fixed a cylindrical tube carrying a lens with about the same aperture and focal distance as the collimator lens. When the instrument was directed towards an aurora, this lens formed a picture which fell on the slit. In this way we ensure that when the optical axis of the collimator is directed on a certain point of an aurora, only light from the nearest surroundings of this direction can enter the instrument. In other words, we are able to analyse separately different parts of an auroral display.

During the evenings and nights of March 11th and 12th I succeeded in taking two pairs of such photograms, one pair each day. The spectrogram corresponding to the bottom edge was obtained with about half an hour's exposure. Near the upper limit the light is fainter and the spectrum was here exposed for about four hours. Still the intensities on the plate of the two spectra were nearly the same. Reproductions of the two pairs of spectrograms are given on Plate X. figs. 1 and 2 for March 11th and 12th respectively:

*a* is the spectrum corresponding to the bottom edge.

*b*        "        "        "        upper limit.

The auroræ used for these exposures were mostly drapery-shaped arcs and some draperies and isolated rays. The bottom edge corresponds to a height of about 100 km. and the two spectra to be compared correspond to a difference of height of about 50–80 km.

The intensities of the spectral lines will be accurately

measured later on by means of a microphotometer, but some results can be directly seen on the plates.

Thus the lines belonging to the line spectrum of nitrogen compared with those of the negative bands seem to be somewhat stronger near the upper limit than near the bottom edge, but the most remarkable result is, that *the intensity of the green line as compared with that of the strong negative N-bands is quite as great near the bottom edge as it is 50-80 km. higher up in the atmosphere.*

If there is a change of relative intensity it is very small indeed, and goes in such a direction as to make the negative N-bands relatively stronger as we pass upwards.

### *Discussion and Results.*

§ 2. In order to make clear the significance of this result we assume the upper strata of the atmosphere to be composed of Nitrogen, Oxygen, Hydrogen, Helium, and Geocoronium in the way given by Wegener, and we shall calculate the ratio of the pressures of H, He, and O to that of nitrogen for various heights. The results are given in Table I. :—

TABLE I.

Height. km.	H/N.	He/N.	O/N.
80	2.7	0.18	0.049
100	45	2.4	0.032
120	760	33.0	0.025

In the case of "Geocoronium," which is supposed to be a gas lighter than hydrogen, the ratio Geoc./N should vary even more than with hydrogen.

It appears from the table that only a comparatively small difference of molecular weight such as that of O and N would produce a considerable change with altitude of the ratio between the pressures of the two gases.

Comparing the numbers of Table I. with the results of our spectral analysis it follows that the green line cannot *be due to any elementary gas different from nitrogen*, provided that the matter in the auroral region exists in a gaseous state. The green line must either be emitted from nitrogen itself or from some substance which in these regions has entered into combination with nitrogen. Here merely compounds with elements lighter than nitrogen can come into consideration, because a compound formed with some heavier element could not keep its place on the top of the ordinary nitrogen atmosphere.

Briefly speaking, of known compounds only  $\text{NH}_3$  could come into consideration. But if the upper strata were composed of  $\text{NH}_3$  we should expect that the auroral spectrum should show the ordinary hydrogen lines with considerable intensity. But as we saw in the first paper this is not the case. The green line cannot be due to a hypothetical gas "Geocoronium" if this gas exists in the elementary form, but we should have to suppose that this gas had a great chemical affinity to nitrogen and thus formed a compound with this gas. An assumption of this kind would quite formally agree with the results of our analysis of the auroral spectrum. It is against our present knowledge with regard to the elements constituting matter, and I think that the "Geocoronium" hypothesis ought to disappear from the scientific literature, and if so the only possible interpretation of our auroral spectral analysis is to assume that also the green line is a nitrogen line emitted under those peculiar physical conditions under which the light is produced in the upper strata of the atmosphere. Later on we shall see what these conditions may possibly be.

As already mentioned the green line is observed to the upper limit of very high rays reaching altitudes of 300–400 km. or more; and as it appears that the ratio between the intensity of the green line and that of the nitrogen lines does not increase as we pass upwards, *it follows, independent of the view we adopt with regard to the origin of the green line, that nitrogen must be a predominant component of the atmosphere to its very extreme upper limit.*

Already in my first communication I was led to the same view, and I gave several arguments in favour of it, but at the same time I mentioned that the correctness of it might be tested by comparing auroral spectra corresponding to different altitudes, and as we see this comparison has shown that the view adopted was the right one.

In the first paper I discussed the consequences of the view, which now is to be regarded as an established fact, that nitrogen is a predominant component of the atmosphere as far up as noticeable auroral light can be observed.

To explain that nitrogen at a height of 500–700 km. could have a sufficient density to give noticeable light emission, we might either assume that above a certain height the temperature increased rapidly upwards or that the nitrogen was electrically charged by photo-electric effect and driven upwards through the effect of the electric field produced by the charged layer.

The assumption of a very high temperature of several

hundred degrees centigrade might quite formally explain the relatively great density of N in the auroral region, but is very unlikely from a physical point of view; and above all such a state of the atmosphere cannot explain the peculiar type of nitrogen spectrum which is emitted from these regions during auroral displays.

An increase of temperature would involve that the amount of matter to be traversed by the cosmic electric rays in order to reach a distance of 100 km. from the ground would be very much greater than the amount of nitrogen which according to Wegener's assumptions should exist above this level.

Referring to earlier investigations with regard to the properties of the rays which may produce the auroræ, we can draw the conclusion that only electron rays could produce the auroræ—provided that we assume a high temperature to exist in the auroral region.

In this case the auroral spectrum, the green line included, should be produced when nitrogen gas of a temperature of some hundred degrees centigrade is bombarded by cathode rays.

In order to test this point I have photographed the spectrum emitted when nitrogen is bombarded by cathode rays at room temperature and at the temperature of liquid air. The result will be seen from Pl. X. fig. 3, where 3a corresponds to room temperature and 3b to the temperature of liquid air.

In fig. 4 of the same plate is given a reproduction of the auroral spectrum obtained by the big glass spectrograph (4b) and a reproduction of a spectrum from the quartz spectrograph (4a).

Apart from the green line, the appearance of which will be discussed later on, the auroral nitrogen spectrum is distinguished by a relatively small number of lines—and although most lines form part of positive or negative bands the greater part of the lines appears fairly sharp and the shades towards shorter wave-lengths are very much suppressed.

Comparing the two N-spectra at different temperatures we see that an increase of temperature is accompanied by an increase of the number of lines and the shades of the bands (number of components in the band series) are also increased with temperature.

While there is a striking similarity between the auroral spectrum and that corresponding to the temperature of liquid air, this similarity is by no means so marked when we compare the auroral spectrum with that corresponding to

room temperature, and when we assume a high temperature in the auroral region there seems to be no possible way open for explaining the appearance of the green line.

*On the Distribution of Matter in an Electrified Atmosphere.*

§ 3. *If now we have to give up the assumption of a high temperature I can see no escape from the assumption that nitrogen in some way or other must be driven upwards through the effect of electric forces.*

This hypothesis introduces the problem of finding how the density of an electrified atmosphere will vary with the height as we pass upwards from the neutral part of the atmosphere.

From the phenomenon of electric wind we are familiar with the idea that an electrically charged gas in an electric field is exposed to the action of a mechanical force, and already in the first paper I assumed that the variation of pressure was given by the equation

$$dp = -(pg - \sigma F)dr, \quad . \quad . \quad . \quad (1)$$

where  $p$  is the pressure,  $\rho$  the density,  $\sigma$  the electric charge per unit volume of the gas,  $F$  the electric force, and  $r$  the distance from the centre of the earth to the point considered.

From this equation we see that the electric charge will have the effect of diminishing the rate of decrease of the density as we pass upwards. If we try to calculate the distribution of matter more accurately we shall soon find that the problem is a somewhat complicated one.

It is my intention to show that under certain assumptions we can find a differential equation for the variation of density with the height, and that we are able to draw some consequences from our hypothesis of an electrically charged upper layer.

Let us suppose the earth to be a perfect sphere and that  $\rho$  and  $\sigma$  are functions of  $r$  only. We apply the theorem of Gauss to a spherical surface through the point  $P$  at a distance  $r$  from the centre of the earth. Then

$$4\pi r^2 F = 4\pi E_r,$$

$$F = \frac{E_r}{r^2}.$$

The total electric charge  $E_r$  inside the sphere is given by

the equation :

$$E_r = E_0 + 4\pi \int_{r_0}^r \sigma r^2 dr,$$

where  $E_0$  is the total charge inside some arbitrary sphere with radius  $r_0$ . Then

$$F = \frac{E_0}{r^2} + \frac{4\pi}{r^2} \int_{r_0}^r \sigma r^2 dr. \quad (2)$$

We suppose that the usual relation between pressure and density of a gas also holds in an electric atmosphere, or that

$$p = \frac{RT}{M} \rho, \quad (3)$$

where  $M$  is the molecular weight and  $R$  the gas constant.

Combining equations (1), (2), and (3) we get :

$$\frac{RT}{M} d\rho = - \left[ \rho g - \frac{\sigma E_0}{r^2} - \frac{4\pi\sigma}{r^2} \int_{r_0}^r \sigma r^2 dr \right] dr.$$

Putting  $\frac{RT}{M} = a$ ,

$$\frac{ar^2}{\sigma} \frac{d\rho}{dr} + \frac{\rho gr^2}{\sigma} - E_0 = 4\pi \int_{r_0}^r \sigma r^2 dr. \quad (4)$$

Differentiating with respect to  $r$  and remembering that  $\rho$  and  $\sigma$  are functions of  $r$ , the equation takes the form :

$$\frac{1}{\sigma} \frac{d^2\rho}{dr^2} - \frac{1}{\sigma^2} \frac{d\sigma}{dr} \frac{d\rho}{dr} + \left( \frac{2}{r} + \frac{g}{a} \right) \frac{1}{\sigma} \frac{d\rho}{dr} - \frac{g\rho}{a\sigma^2} \frac{d\sigma}{dr} + \frac{2g\rho}{a\sigma r} - \frac{4\pi\sigma}{a} = 0. \quad (5a)$$

The equation contains two unknown quantities  $\rho$  and  $\sigma$ , and to solve the problem one equation more is wanted.

This second relation depends on the way in which the atmosphere is brought into its charged state.

In the previous papers it was pointed out that the atmosphere might be positively charged through the photo-electric effect (secondary cathode rays) produced by X- or  $\gamma$ -rays from the sun, but even if this is the only cause of the charged state of the atmosphere we are not in the possession of sufficient data to find the charge given to the atmosphere in this way. Whatever may be the cause of the charged state, we must assume the charge attached to the gas. Thus  $\sigma$  may

be regarded as a function of  $\rho$  and the equation (5) takes the form :

$$\frac{1}{\sigma} \frac{d^2 \rho}{dr^2} - \frac{d\sigma}{d\rho} \left( \frac{1}{\sigma} \frac{d\rho}{dr} \right)^2 + \left( \frac{2}{r} + \frac{g}{a} - \frac{g\rho}{a\sigma} \frac{d\sigma}{d\rho} \right) \frac{1}{\sigma} \frac{d\rho}{dr} + \frac{2g\rho}{ar\sigma} - \frac{4\pi\sigma}{a} = 0. \quad (5b)$$

Now we may always put

$$\sigma = \alpha\rho,$$

where  $\alpha$  is a function of  $\rho$ . And we know that in a great many cases the auroræ have the same colour from the upper limit to the bottom edge. If the auroral region is electrically charged this would indicate that in this region  $\alpha$  should be nearly a constant quantity. We are thus led to consider the case that  $\alpha$  is constant down to a certain distance from the centre  $r_0$ .

Putting this distance equivalent to  $r_0$  in equation (2) it follows that above this distance the density should be determined by the differential equation :

$$\frac{d^2 \rho}{dr^2} - \frac{1}{\rho} \left( \frac{d\rho}{dr} \right)^2 + \frac{2}{r} \frac{d\rho}{dr} + \frac{2g\rho}{ar} - \frac{4\pi\alpha^2\rho^2}{a} = 0. \quad (6)$$

Even under these simplified conditions the differential equation is a rather complicated one, and up to the present I have not been able to find the integral function. But at any rate, we may find the variation of  $\rho$  by means of numerical integration.

#### *On the Possibility of a highly electrified Gas Layer.*

§ 4. Without entering further into the problem of solving the differential equation, we can make some estimates as to the degree of ionization and the amount of electricity which may be present in the higher strata of the atmosphere, and draw some consequences of importance with regard to their state.

We know that the earth—in some way or other—maintains a negative charge, and this charge will be compensated by positive electricity in the atmosphere. This charging process must be continually going on, and we might perhaps suppose that the positive electricity is formed by photo-electric action in the upper layer of the atmosphere. At a certain height the positive electric mass just equals the negative, and on a sphere at this distance the electric force will be zero. Under this niveau the electric force is directed downwards, and



only above it will there be an upwardly directed electric force.

It is only the positive electricity above this zero layer that will be responsible for the electric field of the earth outside the zero sphere.

If the sun emits X- or  $\gamma$ -rays, these rays, when they strike the upper strata of the atmosphere, will cause the gas to emit electrons with a velocity given by Einstein's equation :

$$h\nu = \frac{1}{2}mv^2 = eV. \quad . \quad . \quad . \quad (7)$$

Some of these electrons leave the earth, and this process will continue until the potential of the earth  $V$  is equal to the potential which is determined from the frequency.

If the rays had a wave-length of 1 Å. the potential should be 41 electrostatic units.

At the very limit of the atmosphere, *e. g.*, 600 km. above the ground, there should be an electric force :

$$F = \frac{V}{R} = 6 \cdot 10^{-8} \text{ el.st. units.} \quad . \quad . \quad . \quad (8)$$

Probably there may be a radiation of much shorter wave-length and the electric force would be correspondingly greater.

Now, if we have a nitrogen ion with a positive charge  $+e$ , at the same point, it will be driven upwards with a force  $Fe$  and downwards with the force  $mg$ . If the ion does not leave the earth we must have

$$mg > F \cdot e.$$

Putting

$$m = Mm_H,$$

where  $m_H$  is the mass of a hydrogen atom

$$F < \frac{gM}{3 \cdot 10^{14}} \cdot . \quad . \quad . \quad . \quad (9)$$

If the ion is a charged molecule  $M=28$ , and

$$F < 10^{-10} \text{ el.st. units.}$$

We see that only an extremely small electric force would be sufficient to counterbalance gravity, and the electric force which might be produced through the electron emission due to photo-electric effect is several hundred times larger than that which is necessary to drive a charged molecule away from the earth.

It seems as if the emission of X- and  $\gamma$ -rays from the sun would gradually tap the atmosphere of its nitrogen. This

tapping must be counterbalanced in some way, and the idea naturally suggests itself that the ions are not charged molecules, but at the very low temperature they form clusters consisting of a large number of molecules.

We can also arrive at the same conclusion in another way, by calculating the mass per unit area above the zero sphere. We suppose a cylinder of unit cross-section placed radially and with one end at the surface of the zero sphere and the other reaching outside the atmosphere. Let the mass contained in this cylinder be  $\mu$  and the number of molecules  $n$ . Then

$$\mu = nm.$$

Let us suppose that a fraction  $\beta$  of these molecules carry an elementary charge  $e$ . The total charge  $\epsilon$  in the cylinder would then be

$$\epsilon = \beta ne.$$

Hence

$$\epsilon = \beta \frac{e}{m} \mu. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

As the length of the cylinder is small as compared with the radius of the earth the total electric charge above the zero sphere should be

$$E = 4\pi r^2 \epsilon,$$

and just at the limit of the atmosphere the electric force should be

$$F = \frac{E}{r^2}, \quad \text{or approximately}$$

$$F = 4\pi \epsilon = 4\pi \beta \frac{e}{m} \mu. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

If at the outer limit of the atmosphere the action of the gravitation on unit volume is greater than the mechanical force due to the electric charge we must have :

$$\rho g > \sigma \cdot F. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

Let the number of molecules in unit volume be  $n'$ , then

$$\rho = mn',$$

$$\sigma = \beta' n' e, \quad \text{and}$$

$$\frac{\sigma}{\rho} = \beta' \frac{e}{m}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

$\beta'$  is the ratio of the number of charged molecules to the

total number in unit volume.  $\beta'$  may vary with  $r$ , and thus be different from  $\beta$ , which is an average for the region above a certain level. To get an estimate we will put  $\beta' = \beta$ .

Inserting the expressions for  $\frac{\sigma}{\rho}$  and  $F$ , the condition (12) takes the form

$$g > 4\pi\mu\beta^2\left(\frac{e}{m}\right)^2.$$

Now,

$$\frac{e}{m} = 1.07 \cdot 10^{13}, \text{ and}$$

$$4\pi\beta^2\mu < 10^{-23} \text{ gram.} \quad . \quad . \quad . \quad . \quad . \quad (14)$$

If each molecule carried a charge  $e$ ,  $\beta=1$  and  $4\pi\mu = 10^{-23}$  gram. This would mean that practically no charged matter could exist above the zero sphere. Underneath the zero sphere, however, the electric force is directed downwards, and the electric charge could not account for the density of nitrogen diminishing as slowly as would be necessary to explain the very long auroral ray streamers.

If the upper strata of the atmosphere were in an electrically charged state we should have to assume that  $\beta$  is very small. But at the very low densities it is rather doubtful whether an individual ion of molecular dimensions will impart to the other molecules a mechanical force as if the electric charge had been equally divided on all molecules.

If we shall stick to the hypothesis that nitrogen maintains a noticeable density to heights of 500–600 km. through the effect of electric forces, we must assume that the charged particles form clusters of drops of a very small size. If the temperature is extremely low it seems possible that nitrogen might condense round the ions. We know that the freezing-point of nitrogen is at about  $60^\circ$  Abs., and if the temperature were still lower nitrogen might be present in the form of minute crystals, or fine solid dust.

If the diameters of the drops or dust-particles were of the same order of magnitude as the wave-length of light there might be about  $10^8$  molecules in each particle. In equation (9) we should then have to put  $M=28 \cdot 10^8$ , and in order to prevent the dust-particle from leaving the earth it is only required that :

$$F < 10^{-2} \text{ electrostatic unit,}$$

and this force is much greater than that which would result from photo-electric action from the sun provided the maximum frequency of the rays was  $1 \text{ \AA}$ .

*On the Amount of Matter in the Dust Layer.*

§ 5. If we assume this physical state of the upper strata, we are left rather in uncertainty with regard to the amount of matter which may be present in the auroral region. We can no longer apply the gas laws as expressed in the equations (1) and (3), and the variation of average density of the dust layer is not determined by the differential equation (5).

The dust-particles will be of unequal size and charge, and according as  $\frac{e}{m}F$  is greater or smaller than  $g$ , the particle will move upwards or downwards. A particle that is moving upwards may pick up an electron and thus get its positive charge reduced so that it begins to sink. We have also to reckon with the possibility that some particles that are moving upwards do not pick up electrons and thus leave the earth, and the question arises: is this possibility in some way excluded or is nitrogen in minute quantities continually leaving the earth, and if so, is the nitrogen which is lost replaced by new supplies coming in from space—*e. g.*, from the sun? At present I merely put these questions, which can give room for many speculations and suggestive ideas.

The sinking particles may, some of them, lose electrons and can be caused to move upwards, others may continue to sink till they get vaporized. To re-establish equilibrium equal quantities of gas will move into the dust atmosphere and condense into small drops or crystals.

The density of matter in the gas atmosphere may be approximately estimated. How much matter can be kept up by electric forces, however, is not easily found. It will depend on the intensity and wave-length of those sun-rays which are mainly responsible for the photo-electric action and the ionization; further, the amount of matter will depend on the height of the transition layer between gas and dust atmosphere. From auroral observations we can conclude that this height is less than 100 km.

Through our investigations we are led to a conception with regard to the constitution of the higher strata of the atmosphere fundamentally different from the view earlier adopted among scientists. It has hitherto always been supposed that there was an upper layer of light gases He and H. The composition of the atmosphere according to the

older view is illustrated in fig. 1. The curves are drawn in accordance with Wegener's assumptions. Various authorities differ with regard to temperature and amount of hydrogen and helium, but in any case we should get a distribution of the type given in fig. 1.

Fig. 1.

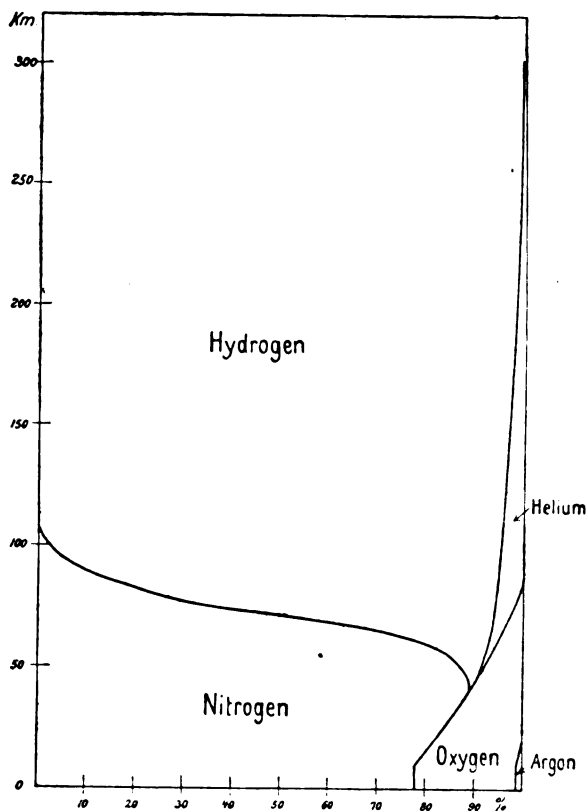
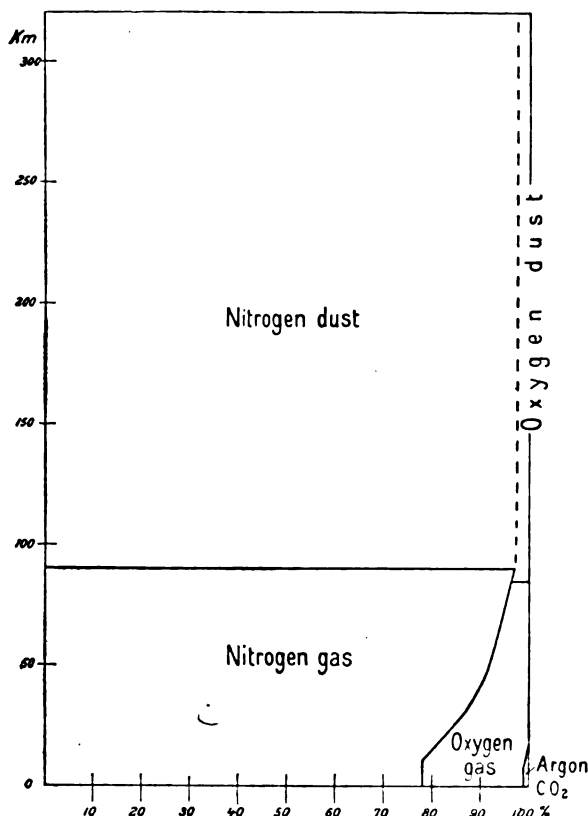


Fig. 2 gives a similar representation of the composition of the atmosphere here found from our investigations on the auroral spectrum. The transition between gas- and dust-atmosphere is indicated at a height of 90 km.

Our view with regard to the physical state of the upper strata of the atmosphere makes it at once intelligible that there can be no hydrogen and helium layer on the top of our atmosphere, for on account of the much lower freezing-point

of the gases they may be unable to form clusters or dust-particles, and as soon as a hydrogen molecule or a helium atom reaches above the sphere of zero electric force it will sooner or later get ionized and fly out of the atmosphere as a positive ray. The distribution of light intensity of the

Fig. 2.



various auroral forms seems to indicate that the dust atmosphere has a comparatively great density in the height interval 100–120 km., but above this interval the average density seems to be very small, but the existence of long auroral rays keeping a nearly constant intensity for a distance of several hundred kilometres shows that the average density in the dust layer above 120 km. only decreases very slowly as we pass upwards.

*The Nature of the Cosmic Electric Rays.*

§ 6. As we are left very much in uncertainty with regard to the amount of matter present in the auroral region we are also left in doubt as to the nature of the rays that produce the auroræ. From the study of the variation of light intensity along the auroral streamers I was able to show\* that the electric rays do not move in nearly straight line tracks but that they must move in spirals round the magnetic lines of force.

From measurements of the thickness of the auroral streamers we then found that the cosmic electric rays had to fulfil the conditions

$$\frac{mv}{e} \approx 10^4. \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Further, we found the range  $x$  in nitrogen at atmospheric pressure to be approximately given by the equation :

$$x = 10^{-27} \frac{M}{n^2} v^3 \text{ cm.} \quad . \quad . \quad . \quad . \quad (16)$$

The ray carrier is supposed to have a mass  $M/N$  and a charge  $ne$ , where  $N$  is Avogadro's number, and  $e$  the elementary charge.

If now the rays fulfil the equation (15) we get

$$x \approx 10^{-3} \frac{n}{M^2} \text{ cm.} \quad . \quad . \quad . \quad . \quad (17)$$

Taking into account our knowledge with regard to the constitution of matter  $\frac{n}{M^2}$  will decrease with increasing mass of the carrier. The amount of nitrogen which, according to the assumptions of Wegener, had to be traversed by a ray reaching a height of 100 km. is equivalent to a layer of 0.2 cm. reduced to atmospheric pressure. In that case only rays of negative electrons could, according to equation (17), give a sufficient penetrating power. For hydrogen nuclei  $n=1$  and  $M=1$ , and equation (17) gives  $x \approx 10^{-3}$  cm., or a hydrogen ray having the sufficient magnetic deflectibility could not reach a height of 100 km., provided that the amount of nitrogen above 100 km. is that assumed by Wegener†.

It will now be understood that since our results with

\* See L. Vegard, *Forhandlinger ved Skandinaviske Geophysikermøtet i Gøteborg*, 28-31 Aug., 1918, p. 12; Vegard and Krogness, *Geophys. Publ.* vol. i. no. 1, p. 159; Vegard, *Phil. Mag.* vol. xlii. p. 59 & p. 79 (1921).

† See L. Vegard, *Phil. Mag.* xlii. Table X. (1921).

regard to the constitution of the upper strata of the atmosphere leave us in doubt with regard to the amount of nitrogen present in the auroral region we cannot conclude that the auroræ are necessarily produced by electron rays.

In any further treatment of the problem we should have to take into account that the absorption does not any longer take place in a gas or in a system which may be regarded as homogeneous. We must, in other words, remember that even if an electric ray is absorbed by a single dust-particle it may have a fairly good chance of getting far down into the dust-layer when the average distance between the particles is fairly large.

Thus we see that the question with regard to the nature of the cosmic rays has come into a new position through the results of our analysis of the auroral spectrum.

### *The Auroral Spectrum.*

§ 7. According to our view with regard to the physical state of the atmosphere, the auroral spectrum should be formed when electric rays penetrate into an atmosphere mainly consisting of small nitrogen crystals which are more or less electrically charged. As each particle consists of a great many molecules only carrying a few elementary charges the spectrum emitted cannot depend essentially on the electric charge. But if these are the conditions under which the auroral spectrum is formed we can understand why a nitrogen spectrum like that given out by the auroræ has never been reproduced in laboratories, for we should then have to bombard solid nitrogen dust with electric rays.

It should be possible to reproduce, at any rate approximately, the conditions of the auroral light emission by cooling nitrogen by means of liquid hydrogen and bombarding the solid nitrogen by canal rays or cathode rays. At the present time I am making preparations for experiments of this kind.

When we consider the upper strata of the atmosphere to consist of dust particles, it might seem possible that also dust-particles of other kinds of matter might be mixed up with the nitrogen particles, and in that way there might be given a possibility of explaining the green auroral line. But such an explanation of the green line is not possible. For on account of the great intensity of the green line, the matter from which it is emitted must be present in relatively large quantities. As hydrogen and helium are excluded, these particles should be formed by some substance with an



atomic weight greater than that of nitrogen. Now some of these particles may lose their charge to such an extent that they sink below the sphere of zero electric force and then they will continue to sink.

Although minute quantities of cosmic dust may exist in the atmosphere we cannot assume them to be present at any height-interval of the auroral region in quantities almost exactly proportional to the number of nitrogen particles. Or the amount of cosmic dust per unit volume at a certain height in the auroral region should be

$$\rho_k(h) = K\rho_N(h),$$

where  $\rho_N(h)$  is the average density of nitrogen at the height  $h$ , and if the cosmic dust is responsible for the auroral line,  $K$  should be nearly independent of  $h$  and  $\rho_k(h)$  and  $\rho_N(h)$  should be of the same order of magnitude. But even if we assumed a constant "current" of cosmic dust falling towards the earth from all directions we could not assume its density to increase downwards in the same way as the density of the nitrogen particles which are continually formed through the condensation of atmospheric nitrogen.

The fact that the ratio of the intensity of the green line to that of the nitrogen bands is nearly independent of altitude shows, I think, that the green line must be interpreted as a nitrogen line, and taking into account the variability of the nitrogen spectrum there is nothing strange in the idea that nitrogen under the conditions present in the higher strata of the atmosphere, when bombarded with electric rays, is caused to emit lines not found under the conditions as yet experimented upon in the laboratories. As already mentioned, that part of the spectrum which by identification of lines has been found to be due to nitrogen is of a very singular type, as the number of lines in the band series are very much reduced.

Now, according to the theory of light-emission given by Bohr, the number of lines in an ordinary line series should increase when the mutual distance between the molecules increases, and the same rule may possibly hold also for band series. If then the gas in the auroral region consisted of free molecules, we should, considering the extremely small density, expect a great many lines in the series. If, however, the molecules are packed together into particles they are not free, and thus we should expect the conditions to be unfavourable for the formation of a large number of lines of the band series, and we should get a type of spectrum like that observed for the auroræ.

*The Change of Colour of the Auroræ.*

§ 8. A most characteristic feature of an auroral display is the sudden varied colour changes. As pointed out in previous papers these changes cannot be explained through a variation of the type of electric rays.

They are not a function of the altitude, for auroral streamers with their bottom edges at the same level may have a different colour and for the same streamer or drapery the colour may undergo sudden changes.

If the cosmic rays are penetrating into an atmosphere consisting of neutral gases, colour changes of this kind are very difficult to explain, and as a possibility I have previously pointed out that colour changes might result from a change of velocity of the electric rays produced when they pass through the atmosphere. Effects of this kind may play a part, but they cannot account for all colour changes.

If the colour changes are to be explained in this way we must assume that ordinarily a large proportion of the electric rays are turned back into space before being completely absorbed.

From laboratory experiments we know that effects of this kind occur when electric rays are retarded on their passage through nitrogen.

When the velocity is reduced the colour turns red. In the auroræ the red colour should correspond to complete absorption and the average colour should be red when a large portion of the rays are completely absorbed.

This explanation, which seems the only one possible for a gaseous state of the auroral region is, however, somewhat artificial and it meets with great difficulties. Thus we should expect that the auroral forms for which the height of the luminosity is small (Arcs) should be red because they must be formed by rays passing nearly parallel with the magnetic lines of force, and therefore they must have a great chance of being completely absorbed. But, as far as my experience goes, the arcs have always the typical greenish-yellow colour.

If the gas was electrified and if the electrification influenced the spectrum we might, as mentioned in my first communication, explain colour changes through changes of electrification of the atmosphere produced by the electric rays. As we have seen, however, a highly ionized layer of ordinary gas cannot exist, and in a dust atmosphere only a very small fraction of the molecules carry an elementary charge, and the electric charge cannot be supposed to produce

any essential change of the spectrum emitted when the particles are struck by electric rays.

The dust atmosphere, however, gives us in another way a new and simple explanation of the colour changes. To understand this we have merely to bear in mind that the typical auroral spectrum with the very prominent green line is produced when electric rays strike nitrogen dust-particles, and that a more ordinary nitrogen spectrum with the well-known prominent red bands is produced when the same rays strike isolated nitrogen molecules.

The first spectrum gives a total colour of the ordinary greenish-yellow type, the latter should produce a red average effect.

When the dust atmosphere is bombarded by very intense corpuscular radiation some particles may partly disintegrate or evaporate, and the disintegrated nitrogen will give the red colour.

According to the degree of disintegration the ratio between the intensities of the two spectral types will change, and in this way we may get a great variety of colours from green to dark red.

From this point of view we should expect that the deviations from the ordinary greenish-yellow colour would be mostly restricted to very intense auroræ with very concentrated narrow ray streamers, because these conditions are favourable for disintegration.

Diffuse and faint auroræ, however, should have the greenish colour. Thus the dust hypothesis leads to consequences in accordance with observations.

If the atmosphere was bombarded by some kind of matter which was able to penetrate into the ordinary gas atmosphere the transition should be marked by a change of colour from greenish-yellow to red. If we could observe the height where this colour change takes place we should be able to fix the lower limit of the dust layer.

Two phenomena, auroræ and meteors, might here come into consideration. If the cosmic electric rays in certain cases had a sufficient penetrating power to reach the gas layer, we should observe auroræ with a red bottom edge. I have only observed an aurora of this type on one occasion (Oct. 11th, 1912, at Bossekop). But we cannot, only from the change of colour from green to red near the bottom edge, conclude that this change marks the transition between dust and gas. To test this point we should have to take parallaxic photographs and measure the height of the bottom edge. If this were of the usual height the colour change could not mark

the transition layer ; only if the bottom edge was found to be situated considerably lower than 100 km. might the change of colour possibly mark the lower limit of the dust atmosphere.

My colleague Professor Schroeter has mentioned to me that when meteors penetrate into the atmosphere and get luminous the light emitted is first greenish white, but then at a certain point of the orbit the colour suddenly turns into red. A possible interpretation of this change is that it marks the transition between the dust- and the gas-atmosphere.

### *The Height of the Dust Atmosphere.*

§ 9. As this dust-atmosphere depends on the solar action we might expect it to be most strongly developed towards the equator. This may at any rate partly account for a very marked difference with regard to the auroræ observed near the auroral zone and those appearing on lower latitudes. As we pass away from the poles the "ray forms" seem to be more frequent and very much higher. This is also confirmed by the most interesting height measurements carried out by Størmer\* at Christiania during recent years.

He finds much greater upper limits for the auroral rays at Christiania than at Bossekop, and it would seem as if the "height of the atmosphere" increased towards the equator.

We should, however, remember that there is another possibility to be taken into consideration. We know that the upper limit of an auroral streamer may vary greatly even at the same place. As shown in previous papers†, these variations are explained through the effect of the magnetic field. When the rays form a finite angle with the lines of force they will turn about them in screw orbits. When the rays come down nearly parallel to the lines of force there will be an intense light near the bottom edge, but passing upwards the luminosity rapidly diminishes and the visible light may only have an extension upwards of 15–20 kilometres.

If a considerable portion of the cosmic rays enters the atmosphere in directions nearly perpendicular to the lines of force, the number of collisions and the light intensity may be considerable very high up in the atmosphere and we get the long ray streamers.

Now it was pointed out in my previous papers‡ that

\* C. Størmer, *C. R.* t. 179, p. 109 (1923).

† *Forhandlinger ved Geofysikermødet i Gøteborg*, Aug. 1918, p. 12 ;

‡ *The Position in Space, etc.* . . . " *Geophys. Publ.* vol. i. 1920, p. 159 ; *Phil. Mag.* xlii. p. 59 (1921).

† *Loc. cit.*

magnetic disturbances would increase the probability for the formation of long ray-streamers, which gave an explanation of the fact that the auroræ having long ray-streamers usually appear at the time when the magnetic storm is most intense.

Now I have also pointed out that the auroræ are carried down to lower latitudes through the effect of the perturbing magnetic fields, and thus we should expect that the chance of the formation of long streamers should be greater at lower latitudes.

In this way we should be able to explain that long rays in comparison with other forms were more frequent at lower latitudes.

It is, however, not only so that an aurora at lower latitudes has a great tendency to form long ray-streamers, but the considerable material of height measurements obtained up to the present time seems to show that the *maximum height obtainable* is greater at lower latitudes than near the auroral zone.

In the material of 434 pairs of photographs from the Haldde Observatory \* no ray was found reaching a height greater than 303 km. and Størmer's † measurements from the same locality have given a similar result. At Christiania, however, Størmer ‡ finds much higher values for the upper limit. Rays reaching heights of 500 km. are not infrequent, and he has measured heights as large as 750 km.

If the distribution of matter in the auroral region were independent of the latitude we should expect that also near the auroral zone the conditions might sometimes be favourable for the formation of the very long rays. If such very long rays *never* occurred at these localities it would indicate that the height at which the density of the atmosphere falls below a certain value necessary for giving noticeable light emission should increase towards lower latitudes.

As already mentioned, such a variation of the heights of the atmosphere might be due to the variation of the solar action, but I think that also the magnetic field of the earth may act in a similar way. The electric particles will, during their upward motion, have a tendency to follow the magnetic lines of force and thus the electrified "dust" may be driven towards the plane of the magnetic equator of the earth.

Birkeland has made a most interesting experiment which

\* Geophys. Publ. vol. i. no. 1.

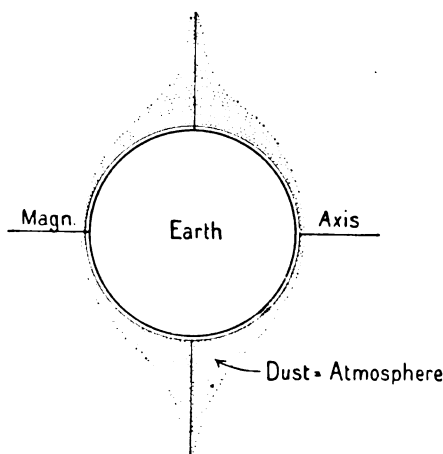
† Geophys. Publ. vol. i. no. 5.

‡ C. Størmer, *C. R.* t. 176, p. 109 (1923).

forms an analogy to this process. When an electric discharge is passing through a discharge tube with a magnetized sphere as a cathode, the discharge is almost entirely restricted to the region near the magnetic equator. The motion of the electrified corpuscles is on both sides directed towards the magnetic equator through the action of the magnetic lines of force. At the plane of the magnetic equator the particles will accumulate and work their way outwards perpendicular to the magnetic lines of force, driven by the electric field.

From the point of view here taken with regard to the constitution of the upper strata of the atmosphere we might

Fig. 3.



expect that the clusters would accumulate near the plane of the magnetic equator, where this dust atmosphere would reach a maximum height, and thus there might be formed a kind of dust ring round the earth as indicated in fig. 3.

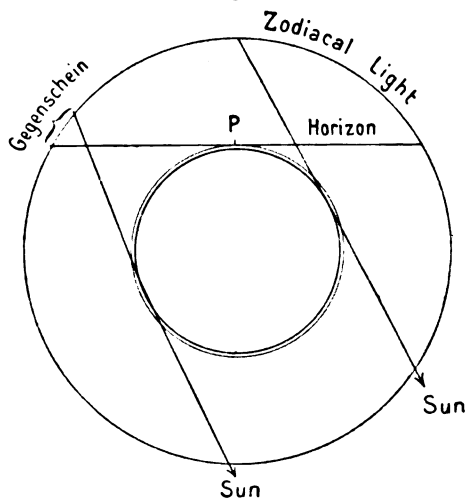
In this connexion it is of interest to notice that probably currents of negative corpuscles from the sun continually circulate round the magnetic equator. When the positively charged particles are driven upwards in the equatorial regions they may meet this swarm of corpuscles and in this way get neutralised so that they again begin to fall.

These equatorial currents of negative electricity might then act as a shield, preventing nitrogen from leaving the earth.

§ 10. The dust ring described in the previous paragraph will scatter the sunlight, and such a disk of small particles is just wanted to explain the zodiacal light. Long after sunset the sun will still illuminate this dust ring, and at places near the equator we see a cone of light standing up from the horizon.

If the disk reaches to a height of the same order of magnitude as the diameter of the earth we may see the luminosity on the other side of the earth (opposite to the sun) in the form of what is called "Gegenschein." (Fig. 4.)

Fig. 4.



As this dust ring is composed of electrified particles in motion it is maintained through a continuous process, and it is to be expected that the dust ring and the zodiacal lights will not be always equally strong even at the same place and under the same light-conditions. It is even possible that fairly sudden changes may occur with regard to the intensity and outlines of the zodiacal light. Indeed, some observers, *e. g.*, von Humboldt and the Rev. George Jones, state that they have noticed very marked changes in the intensity of the zodiacal lights.

Although one of Birkeland's experiments, as we saw, is of interest as an analogy to illustrate the way in which matter is distributed in the upper strata of the atmosphere, still the

explanation here given for the zodiacal light is essentially different from that of Birkeland. According to his view, the zodiacal light should be explained in a similar way as the northlights as a direct effect of radiation from the sun, the two phenomena being produced however by different groups of rays.

The question now might naturally arise whether the ring of Saturn might not be a system of electrical dust formed in a similar way as the assumed dust-ring round the earth? If so, it would follow that Saturn must have an atmosphere and a magnetic field, but the question then arises, why have not the other planets such dust rings? Several circumstances might prevent their formation so, e. g. :

- (1) The temperature may be too high for the formation of clusters.
- (2) The atmosphere might consist of hydrogen and helium which might have a too low freezing-point for the formation of clusters.
- (3) The planet might have no atmosphere.
- (4) The planet might have too weak a magnetic field.

I shall leave these suggestions for the astronomers.

There are, however, some other points in connexion with this view with regard to the constitution of the upper strata of the atmosphere which call for considerable attention.

We have already mentioned that the dust atmosphere scatters the light. If the particles have a suitable average size the light will be selectively scattered, and the upper atmosphere, when illuminated by the sun, would seem to give out light of some colour. In this way I think we may explain the blue sky.

*The blue sky then should be formed through the scattering of sunlight in the nitrogen dust layer which forms the upper strata of the atmosphere.*

Simple every day experiences show that the blue sky cannot be due to scattering of sunlight in a nitrogen gas layer. The amount of gas above each unit of surface is equivalent to the quantity contained in a horizontal cylinder of unit cross-section and with a length of about 10 km. Now if it were not for the atmospheric scattering the sky should appear black in between the stars. But on a clear sunny day a black object at a distance of 10 km. appears very nearly black.

The fact that the sky is quite as blue on the top of very high mountains as near the ground shows that the great scattering resulting in the intense blue colour of the sky



must originate from a layer situated high up in the atmosphere. A continual current towards the earth of cosmic dust cannot come into consideration, for this dust cannot have a greater density high up in the atmosphere than lower down.

In the nitrogen dust, however, we have an inexhaustible source of scattering particles which can never reach below a certain height.

The density of the dust layer is very small, and the average distance between the particles comparatively great. If we drew a line through the dust atmosphere it might only cut a few particles and this number might undergo considerable and rapid changes. In this way the dust layer gives us a very simple explanation of the twinkling of the fixed stars. When we look upon a fixed star with the eye, it is the average intensity through a cylinder with a cross-section equal to the pupil of the eye which determines the observed light intensity. Inside such a narrow cylinder the number of scattering particles may undergo considerable variations, and these variations are seen as twinkling.

If, however, we look at a planet the latter has a measurable angular diameter of say  $8-10''$ , and as the scattering layer is situated so high up in the atmosphere the cone of light reaching the eye will now, in the scattering layer, have a very considerable cross-section of say 20–80 square metres, or  $4 \cdot 10^6-16 \cdot 10^6$  times larger than in the case of fixed stars. The variation of the number of scattering particles inside the cone relative to the total number will now be extremely small and can no longer be observed; the planets give no twinkling.

#### *Concluding Remarks.*

§ 11. If the electrically charged atmosphere were evenly distributed all round the earth it could have *no* influence on the electric field near the ground. If, however, there is an accumulation of charged particles near the magnetic equator there will be an action inwards, and the earth will be negatively charged from electrostatic induction. In this way our electrical atmosphere might to some extent influence the electric field near the surface of the earth.

The electric field of the earth will also act on the electric rays coming from the sun and modify their orbits. Negative rays will be attracted and may reach the earth further from the magnetic poles than they would have done if only magnetic forces had been acting. In this way it seems possible that even electron rays of a moderate penetrating power may come down to the earth in the auroral zone.

During strong auroral displays we often observe that the sky remains luminous for several minutes after the bombardment of the atmosphere by electric rays has ceased. And sometimes it seems as if there were secondary discharges from the part of the sky exposed to the rays. These phenomena are difficult to explain when we assume the rays to penetrate into a gas atmosphere, but if the charge is taken up by dust particles we may understand that it takes a considerable time for the charge to distribute itself.

As the ordinary gas atmosphere is bounded by a dust atmosphere of quite different mechanical and electrical properties the upper layer will reflect sound waves and may act as a shield for electric wave energy. In other words the electrified dust atmosphere forms the "Heaviside layer" round the earth.

As already mentioned, a most characteristic feature of the northlight spectrum is the great reduction in the number of lines. A few of the N-lines are very strong and a few new ones appear—but most of the lines are suppressed.

Now we know also that spectra of nebulae have a similar character; they consist of a few lines, many of which are not found among the lines observed in laboratories. This similarity would suggest a similar constitution of the nebula and the upper strata of the atmosphere, and if our view with regard to the constitution of the auroral region is the right one it would suggest that the nebulae consisted of fine dust particles made luminous through the bombardment of electric rays. These electric rays might be due to disintegration of radioactive matter. If the average density of the nebula is very small the temperature, in spite of some radioactivity, may be very low, just as we have supposed to be the case in the higher strata of the atmosphere.

### § 12. *Summary.*

- (1) Photographs of auroral spectra corresponding to different altitudes have been obtained.
- (2) The intensity of the green line relative to that of the nitrogen bands does not increase as we pass upwards, but shows a small but noticeable diminution.
- (3) Our observations show that the green line cannot be due to any light elementary gas such as H, He, or the hypothetical geocoronium.
- (4) The green line must originate from nitrogen or from some substance attached in some way to nitrogen. Arguments are given for considering the latter possibility to be excluded.

- (5) Independent of any hypothesis with regard to the origin of the green line, observations show that nitrogen is a prominent component of the atmosphere to its very upper limits.
- (6) To explain this fact we must either assume for the auroral region an increasing temperature amounting to several hundred degrees centigrade or we must assume that nitrogen is kept up by the effect of electric forces. Various circumstances seem to exclude the first possibility.
- (7) The differential equation for the variation of density in an electrified atmosphere has been found, but its solution has not been carried farther because some simple calculations have shown that a highly electrified upper gas layer cannot exist.
- (8) If we are sticking to the hypothesis that nitrogen is driven upwards by electric forces we are led to the assumption that the nitrogen in the upper layer is condensed into small crystal particles, which are then electrified through the photo-electric effect of sun-rays of very short wave-lengths.
- (9) The auroral spectrum should be produced when electric rays from the sun penetrate into the layer of nitrogen dust.
- (10) The colour changes of the auroræ are explained through disintegration or evaporation of the dust particles caused by the cosmic electric rays.
- (11) Our view with regard to the physical state of the atmosphere gives a simple explanation of the following phenomena :
  - (a) The sudden change of colour along the track of a meteor.
  - (b) The increase of the maximum height of auroral rays as we pass towards lower latitudes.
  - (c) The zodiacal light.
  - (d) The blue colour of the sky.
  - (e) The twinkling of fixed stars and the absence of twinkling in the case of planets.
  - (f) Reflexion of electric waves and sound waves from the upper layer of the atmosphere.
  - (g) The secondary auroral phenomena.
  - (h) The absence of an upper layer consisting of the light gases hydrogen and helium.

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University, Christiania.

LXV. *On a Simple Method of extending the Balmer Series of Hydrogen in a Vacuum Tube.* By R. WHIDDINGTON, M.A., D.Sc., *Cavendish Professor of Physics in the University of Leeds* \*.

IT is well known that under the usual conditions of the vacuum-tube discharge in the laboratory the hydrogen primary spectrum is limited to only a few lines, ordinarily  $\alpha$ ,  $\beta$ ,  $\gamma$ , and  $\delta$ † only showing with any intensity. This, when contrasted with the fact that in stellar spectra the series is complete, appears in rather a remarkable light.

It occurred to me that in stellar spectra the conditions under which the hydrogen exists may possibly often differ from the state in a vacuum tube in, at any rate, two respects :—

- (1) In being at a much lower pressure.
- (2) In being bombarded continuously and intensely by electrons from the hot interior of the star.

Either of these conditions would favour the production of the primary spectrum rather than the secondary, and moreover should increase the probability of the production of those frequencies nearer the head of the series. The first condition on account of the comparative isolation of the radiating atom and the consequent realization of its possible outer orbits, and the second condition because of the greater opportunity of combination of the positive hydrogen ion with an electron rather than a negative hydrogen ion.

Unfortunately I have not been able to devise a means in the laboratory of realizing conditions (1) and (2) quite separately, but I have had some partial success.

The experiment was perfectly simple, and consisted merely in making a glass vacuum tube fitted with a hot cathode of tungsten wire. Evacuation was effected by an oil backing pump and a mercury diffusion pump, the usual very low vacua being attained with the customary ease. As was expected, when the cathode was cold the discharge refused to pass brightly with a steady stream of electrolytic hydrogen passing through when the pressure fell below a fraction of a millimetre. Photographs with the discharge brilliantly passing at a millimetre or so were taken with a large Hilger

\* Communicated by the Author.

† R. W. Wood (Phil. Mag. 1921) has described a laboratory method of working which provides a much extended series.

quartz spectrograph, and showed, as usual, strong secondary spectrum and the first four members of the Balmer series with intensity rapidly diminishing from  $\alpha$  to  $\delta$ .

Increase of current up to the limit set by the generator furnishing the potential failed to change appreciably the relative intensity of these lines.

The hydrogen supply was now gradually cut down until the pressure fell to below 1000 mm. of mercury or thereabouts. The discharge now refused to pass with the cathode cold, even with an induction coil attached to the tube, only a green glow on the glass showing. When, however, the cathode was brightly glowing, a brilliant discharge passed at this low pressure, a current of several hundred milliamperes being possible if desired.

On photographing this discharge it was found that the intensity of the Balmer series was increased relative to the secondary spectrum, and, more than that, a considerable number of Balmer lines extending into the violet appeared on the plate.

Very unfortunately the dispersion of the spectrograph near the head of the series was not great enough to follow the series very far with absolute certainty, but 19 or 20 members of the primary series were traced confidently with the help of a comparison iron arc spectrum. Further, the relative intensities of  $\delta$  to  $\gamma$ ,  $\gamma$  to  $\beta$ , and  $\beta$  to  $\alpha$  were enormously increased.

How much of this extraordinary change in the intensity of the primary spectrum is due to condition (1) and how much to condition (2) I can only suggest by referring to another observation which was made when examining the tube with the cathode cold, using a small direct-vision spectroscope. I do not remember seeing any reference to this in the literature, but feel sure the phenomenon must be a familiar one to spectroscopists.

It was observed that near the cathode within the dark space the secondary spectrum was absent entirely, only the primary appearing. It is tempting to suggest that this is because the region is rich in electrons, and that the positive ions approaching the cathode have here a greater chance of picking up an electron than a negative ion, with the resulting production of primary rather than secondary spectrum.

The tube was usually supplied with potential from a direct current generator or from cells, and it was interesting to observe again the old phenomenon of regular oscillations of the current in spite of the steadiness of applied potential.

These oscillations were studied in a general manner some

20 or 30 years ago by a number of workers, and their existence has been demonstrated again in a novel manner by Dr. Appleton quite recently.

By viewing the discharge when oscillating in a specially designed high-speed rotating mirror, I have found that the oscillations often co-exist with two systems of flashes travelling through the tube with different speeds in opposite directions, but occurring at regular intervals. More particularly in argon this phenomenon is well marked, and the different colour of the flashes suggests that we have here different spectra probably due to the positive and negative ions respectively. These experiments are being followed up.

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LXVI. *Note on the Ultramicrometer used as a Differential Micromanometer.* By R. WHIDDINGTON, M.A., D.Sc., Cavendish Professor of Physics, and A. HARE, M.Sc., Assistant Demonstrator in Physics, University of Leeds\*.

THE ultramicrometer was first described by one of us in 1920 †, and some of its applications carried out in the laboratory of this University described by Whiddington ‡ and by Sucksmith §.

The application to be noted now makes use of the same valve circuits with unimportant modifications already published. It should be added that Dowling has put on record another means for observing the change in separation of the ultramicrometer plates ||. The heterodyne beat method, however, is considered preferable for many purposes, and whatever can be done by this method can also be done by any of the numerous possible variations of galvanometric methods.

Since the ultramanometer itself is only intended for observing changes of length in its application to the measurement of pressure, it will generally function not as an absolute, but only as a differential manometer.

#### *Previous Instruments.*

An excellent account of the various types of micromanometer so far devised is to be found in the 'Dictionary of Applied Physics,' vol. iii.

This being a readily accessible source of information, it is

\* Communicated by the Authors.

† Phil Mag. Nov. 1920.

‡ Brit. Assoc. 1921.

§ Phil. Mag. Jan. 1922.

|| Proc. Roy. Dub. 1921. Phil. Mag. July 1923.

hardly necessary to do more than mention the fact that the most sensitive manometers hitherto used measure a pressure difference of the order of  $10^{-6}$  mm. of mercury, but are very much less sensitive when the absolute value of the pressure used exceeds  $10^{-3}$  mm. of mercury.

The less sensitive type available for use at pressures approximately atmospheric have a sensitiveness much less—about  $10^{-4}$  mm. of mercury.

The present arrangement, fitted up in a rather crude form, easily gave a sensitiveness much greater than that of the last-named apparatus, and exceeded detection of changes no less than  $7 \times 10^{-6}$  mm. of mercury at ordinary atmospheric pressures.

#### *The Apparatus.*

An ordinary aneroid barometer was taken, and in place of the pointer a small condenser plate was fitted which, as the pressure varied, altered the capacity in the ultramicrometer circuit.

In order to estimate the pressure variations corresponding to observed frequency changes, the instrument was enclosed in a large air-tight bell-jar of about 16 litres capacity, connected by a tube to a mercury column whose height could be varied by known and measurable amounts. From a knowledge of the cross-section of the mercury column and the effective volume of the bell-jar containing the apparatus, the change in internal pressure corresponding to any known change in height of the mercury column could be calculated.

In this way it was found easily possible to observe pressure changes of only  $7 \times 10^{-6}$  mm. of mercury. The usual electrostatic screening precautions were taken, the whole apparatus was rubber-suspended to eliminate shocks, and special oil-damping vanes were fitted on to the recording arm of the aneroid itself.

It is expected that several hundred times this sensitiveness will easily be attained by attaching the ultramicrometer to one of the more sensitive types of micromanometer as, for example, the collodion diaphragm gauge of M. Lafay.

It is clear, in fact, that the ultramicrometer is an attachment which can be fitted to any moving instrument, and performs the function of an amplifier of very great power. Further applications are in progress\*.

The Physics Laboratories,  
The University of Leeds.

\* A highly sensitive microbalance has been under development now for nearly two years, and an experiment on the Michelson Morley lines, giving a negative result, will be noted shortly.

LXVII. *The Value of the Energy Relation in the Testing of Ferrous Metals at Varying Ranges of Stress and at Intermediate and High Temperatures.* By T. M. JASPER, Assistant Professor of Engineering Materials and Engineer of Tests, Fatigue of Metals Investigation, University of Illinois\*.

IT has become desirable that more complete information should be secured for the static, elastic, and fatigue properties of metals at high temperatures. For ferrous metals a considerable number of results have been obtained on the variation of the elastic limit, yield point, and ultimate strength, but very little has been done in applying these results to metals under repeated stress at high temperatures. The application of the effect of high temperatures to repeated stress would materially assist the designer and user of steam turbines and high-speed internal-combustion engines.

In experiments on completely reversed repeated stress there seems to be a close correlation of the first order between the limit of endurance of a ferrous metal and the elastic limit, yield point, and ultimate strength when the rotating-beam method of testing is considered and if the state of the steel is comparable. In experiments on repeated stress with various ratios of reversal there is no simple correlation between the limit of endurance and the static properties of the material above mentioned.

Professor Goodman † in his tests on steels has developed a diagram showing the relation between the range of stress when repeated on a steel and the maximum stress that can be carried successfully an indefinitely large number of times. As the range of repeated stress is decreased, the maximum stress that can be carried is increased. (See fig. 1.)

The investigators working on the Fatigue of Metals at the University of Illinois are able to check the diagram of Goodman for normalized steels for a considerable range, but when heat-treated steels are considered in which the elastic-limit and yield-point values approach proportionally nearer the ultimate strength, the limits of endurance found do not follow Goodman's diagram with a good degree of correlation. Moreover, the upper limit of the range rarely goes beyond

\* Communicated by Dr. W. Rosenhain, F.R.S.

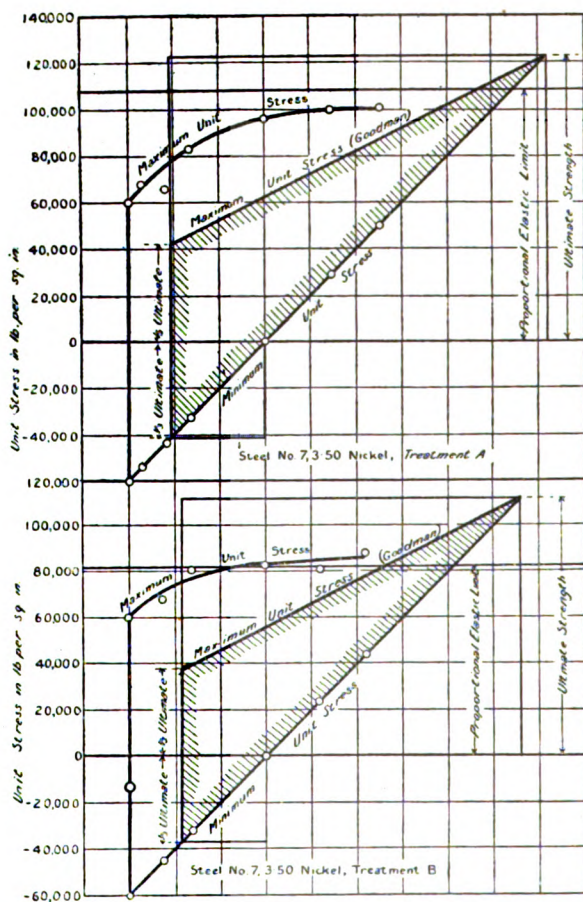
† J. Goodman, 'Mechanics Applied to Engineering,' Longmans, Green & Co., 1918.



the yield point of the material. This is brought out by tests on typical normalized and heat-treated steels shown in fig. 1.

Investigations of the value of the energy relation in testing have brought out the possibility of an application of this

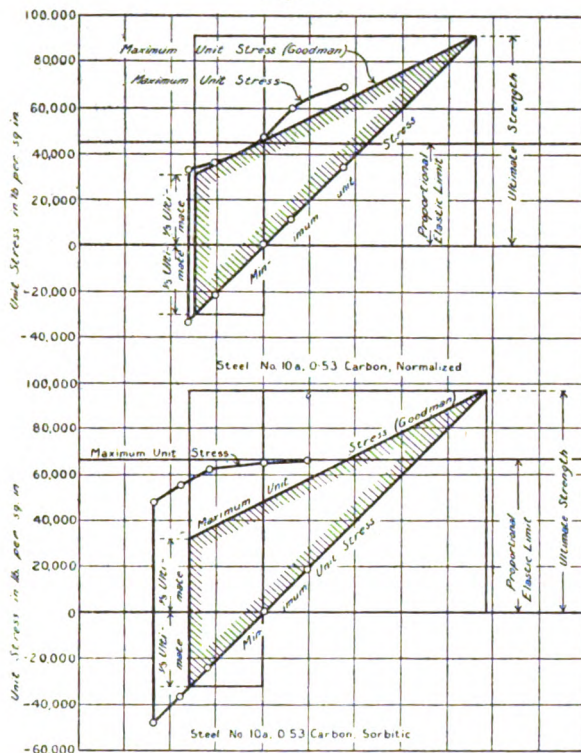
Fig. 1 a.



Curves showing the effect of Range of Stress on the Endurance Limit.

principle to fatigue testing at ordinary temperatures and static testing at higher temperatures, and have suggested the application of this principle to fatigue testing at higher temperatures

Fig. 1 b.



Curves showing the effect of Range of Stress on the Endurance Limit.

### *Development of the Energy Equation with Reference to Testing.*

In the testing of isotropic materials the point at which the energy absorbed per unit volume becomes largest is somewhere at a surface, and is always associated with boundary conditions.

Whatever the stress system may be, it can be shown that the energy relations at a point contained within the material may be expressed by the equation\* :

$$W = \frac{\lambda + 2F}{2} (\epsilon_x + \epsilon_y + \epsilon_z)^2 + \frac{F}{2} (\epsilon_{xy}^2 + \epsilon_{yz}^2 + \epsilon_{zx}^2 - 4\epsilon_y\epsilon_z - 4\epsilon_z\epsilon_x - 4\epsilon_x\epsilon_y), \quad \dots (1)$$

where  $\epsilon_x$ ,  $\epsilon_y$ , and  $\epsilon_z$  are unit direct extensions along any  $x$ ,  $y$ ,

\* Love, 'The Mathematical Theory of Elasticity,' Arts. 68 & 69, 1920 edition.

and  $z$  axes,  $\epsilon_{xy}$ ,  $\epsilon_{yz}$ , and  $\epsilon_{zx}$  are unit torsional extensions appropriate to these axes,  $\lambda$  and  $F$  are elastic constants, and  $W$  is the energy absorbed per unit volume.

In the development of the elastic theory in isotropic materials the  $x$ ,  $y$ , and  $z$  axes can be so chosen that  $\epsilon_{xy}$ ,  $\epsilon_{yz}$ , and  $\epsilon_{zx}$  are zero, and for this condition equation (1) becomes :

$$W = \frac{\lambda + 2F}{2} (\epsilon_x + \epsilon_y + \epsilon_z)^2 - 2F(\epsilon_x\epsilon_y + \epsilon_y\epsilon_z + \epsilon_z\epsilon_x). \quad (2)$$

The relations existing between the strain and stress are indicated by the following equation :

$$\left. \begin{aligned} \epsilon_x &= \{Sx - \rho(Sy + Sz)\} \frac{1}{E}, \\ \epsilon_y &= \{Sy - \rho(Sz + Sx)\} \frac{1}{E}, \\ \epsilon_z &= \{Sz - \rho(Sy + Sx)\} \frac{1}{E}, \end{aligned} \right\} \dots \dots \dots (3)$$

where  $Sx$ ,  $Sy$ , and  $Sz$  are the values of the principal stresses in the principal  $x$ ,  $y$ , and  $z$  directions,  $\rho$  is Poisson's ratio, and  $E$  the modulus of elasticity in direct stress for the material in question.

In static testing the conditions aimed at are to get simple tension, compression, or torsion in the surface of the material where the maximum stresses are developed. If substitutions from equation (3) are made in equation (2), and providing it is understood that with the exception of the case of a sharp re-entrant angle there are only two principal stresses possible on a boundary, and that in the ordinary method of testing in tension or compression only one principal stress need be considered, the following relations are obtained :

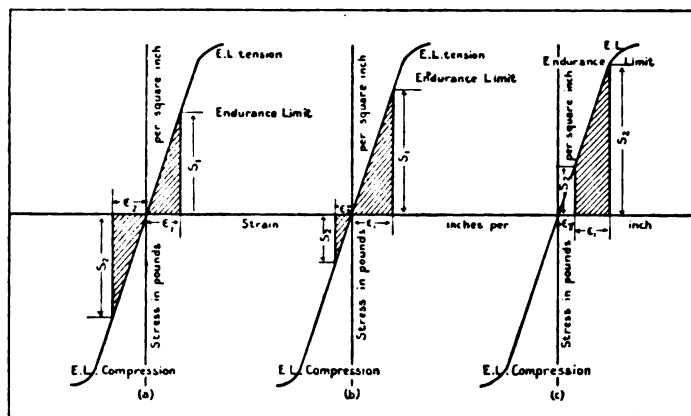
$$\left. \begin{aligned} \text{Simple Torsion} \dots\dots W &= C_1 \frac{S_{x_a}^2}{2F}, \\ \left. \begin{aligned} \text{Simple Tension or} \\ \text{Compression} \dots\dots \end{aligned} \right\} W &= C_2 \frac{S_{x_b}^2}{2E}, \end{aligned} \right\} \dots \dots \dots (4)$$

where  $S_{x_a}$  is the maximum stress in torsion and  $S_{x_b}$  is the stress in tension or compression,  $C_1$  and  $C_2$  are constants, the values of which are very nearly 1, and  $F$  and  $E$  are the moduli of elasticity in torsion and tension, respectively. It must be understood that the discussion applies strictly within the range where the stress is proportional to the strain.

In the testing of ferrous metals in fatigue at ordinary temperatures, it has become apparent that the energy per unit absorbed by the material at the most stressed point is

very close to a constant value. This relation applies generally to the conditions where the stress is completely or only partially reversed, provided the yield point is not exceeded. It also applies equally well, when the energy value is known, to reversed torsion, reversed direct stress, or reversed-bending results. See fig. 2.

Fig. 2.



Curves showing graphically the value of the energy relation as applied to simple tension or compression in reversed stress tests.

In the above figure,

$S_1$  = Stress per unit area, maximum ;

$S_2$  = Stress per unit area, minimum ;

$\epsilon_1$  = Strain per unit corresponding to  $S_1$  ;

$\epsilon_2$  = Strain per unit corresponding to  $S_2$ .

In referring to fig. 2 (a) the amount of energy involved per unit for complete reversal of stress at the endurance limit is represented by the following equation :

$$W = \frac{1}{2} (S_1 \epsilon_1 + S_2 \epsilon_2), \quad \dots \dots \dots (5)$$

where  $W$  is the energy involved per unit of volume per cycle of stress. The unit involved is essentially inch-pounds per cubic inch, for in equation (5)  $S$  is measured in pounds per square inch and  $\epsilon$  in inches per inch. Multiplying these together gives the value in inch-pounds per cubic inch. If within the elastic limit of the material for the case of tension

or compression  $\epsilon_1$  and  $\epsilon_2$  are equivalent to  $\frac{S_1}{E}$  and  $\frac{S_2}{E}$  respectively, where  $E$  is the modulus of elasticity, and  $S$  the

stress per unit area, and if the values of  $\epsilon_1$  and  $\epsilon_2$  thus obtained in equation (5) are substituted, the energy involved becomes

$$W = \frac{1}{2E} (S_1^2 + S_2^2). \quad \dots \dots \dots (6)$$

If the cycle does not involve a reversal of stress, the above relation becomes (see fig. 2 (c))

$$W = \frac{1}{2E} (S_1^2 - S_2^2), \quad \dots \dots \dots (6a)$$

and in this case  $S_1$  and  $S_2$  are both values in tension or both in compression, as the case may be, or  $S_2$  is equal to zero. For a complete reversal of stress, equation (6) becomes

$$W = \frac{S^2}{E} \quad \dots \dots \dots (6b)$$

The term *endurance limit* has been used. For a ferrous metal, in the laboratory of the Fatigue of Metals at the University of Illinois, the endurance limit is taken to represent the maximum value of stress that a metal can withstand in repeated stress for an indefinitely large number of cycles. If a ferrous metal in repeated stress is run at a stress a very small per cent. above the endurance limit, it will usually fail before it has reached 2,000,000 cycles. If a ferrous metal is repeatedly stressed at or below the endurance limit, it will withstand at least 100,000,000 cycles of stress without failure. The time involved in experimenting beyond this point has induced the laboratory to withdraw the specimens at 100,000,000 cycles without failure\*. A few experiments have been run, however, where the number of cycles have exceeded 900,000,000 at the endurance limit stress.

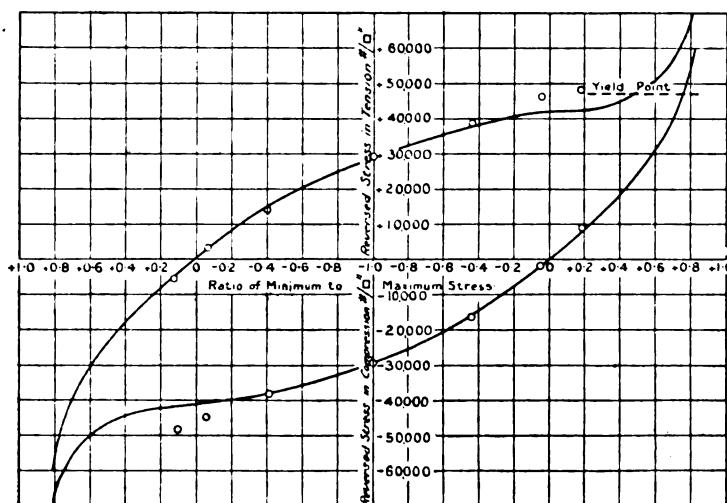
It cannot be assumed, from the nature of the stress-strain relations, that for a ferrous metal the energy constant will hold above the static yield point of the material, although in the laboratory values in some instances above this point as maximum values are obtained for endurance limits. This is explained by the fact that the yield point is probably raised by cold-working in the direction of the maximum stress in fatigue and has been verified by static tests on specimens after they have been removed unbroken from the fatigue-testing machines, the specimens having run 100,000,000 cycles without failure.

The application of equation (6) has been made to the

\* H. F. Moore & T. M. Jasper, "An Investigation of the Fatigue of Metals," Series of 1923, Urbana, Ill. Eng. Exp. Sta. Bulletin No. 136.

variation of range of stress in the following manner:—The endurance limit for a complete reversal of stress has been substituted in equation (6 b), and the value of  $W$  established for a particular steel. With the value of the energy for any steel known, if progressive values of  $S_1$  are assumed and the unassumed values of  $S_2$  are calculated, a curve can be drawn which is shown in fig. 3.

Fig. 3.



Curve showing the value  $W = \frac{S_1^2 + S_2^2}{2E}$  assuming that at complete reversal the value is given by  $\frac{S^2}{E}$ .

The plotted points are from experiments by B. P. Haigh.

This curve can be called the hypothetical curve for the material in question and for the particular type of stress involved. The experimental values of the endurance limit for partially reversed repeated stress have been plotted on this curve with the result as shown\*. The coordinate along the X-axis represents the ratio of the minimum stress values divided by the maximum stress values, and the coordinate on the Y-axis represents actual stress values. This method has been adopted for endurance limits involving

\* These experimental values were taken from results published by Bernard P. Haigh for Mild Steel. "The Endurance of Metals under Alternating Stresses," read before the West of Scotland Iron and Steel Institute, Nov. 1915.

torsional, direct, and bending stresses. The maximum stresses in bending with a rotating cylinder are either tension or compression, but it has been found that the rotating-beam tests for normalized or annealed steels give values about one-sixth higher than those obtained for the direct stress values when considering any particular steel. In the case of torsion, the appropriate value of the elastic constant involved is necessary if the torsional endurance limits are to be compared with the bending endurance limits. It will be noticed that the experimental values follow very closely the curve as outlined. See also fig. 1, Goodman's diagram, and the results from the laboratory of the Fatigue of Metals, University of Illinois\*.

#### *Testing Materials at Various Temperatures.*

With the foregoing discussion in mind, the necessity for knowing the value of certain elastic properties of steel at varying temperatures presents itself, if the results at ordinary temperatures are to be applied to a steel at temperatures above the ordinary. This involves obtaining the appropriate values of  $E$  the modulus of elasticity and  $F$  the modulus of shear or rigidity, as it is often called, for each temperature considered.

It is to be hoped that experimental values of the endurance limits for several steels under varying temperatures may be obtained. This will mean, however, multiplying the work necessary for obtaining an endurance limit for a steel at the ordinary temperature by the number of different temperatures involved, and by a factor commensurate with the difficulty of maintaining such temperatures. The purpose of this part of the paper, therefore, is to stimulate thought on the question, to offer the results of the author's studies and experiences, to correlate some of the work done by other investigators on the question, and to apply this discussion to static experimental values at varying temperatures in which case results are already available.

The most complete work accomplished to date with reference to the variation of  $E$  the modulus of elasticity, and  $F$  the modulus of shear with varying temperatures is by Wm. Sutherland†, and for the development of the relation found by him reference is made to his publication. The following fundamental equation for rigidity has been

\* F. M. Howell, Asst. Engineer, Investigation of the Fatigue of Metals, Chap. iv. "An Investigation of the Fatigue of Metals," University of Illinois Eng. Exp. Sta. Bulletin 136.

† Wm. Sutherland, "Kinetic Theory of Solids," Phil. Mag. 1891.



borrowed from Sutherland and applied identically in the manner adopted by him. To this have been added several other experimental values obtained for ferrous metals with the result as shown in fig. 4. The equation is as follows:

$$\frac{F}{F_0} = 1 - \left( \frac{T}{T_m} \right)^2, \dots \dots \dots (7)$$

where

$F$  = the modulus of shear at any temperature absolute,

$F_0$  = the modulus of shear at zero temperature absolute,

$T$  = the temperature absolute at which  $F$  is obtained,

$T_m$  = temperature absolute at which the metal melts.

Fig. 4.

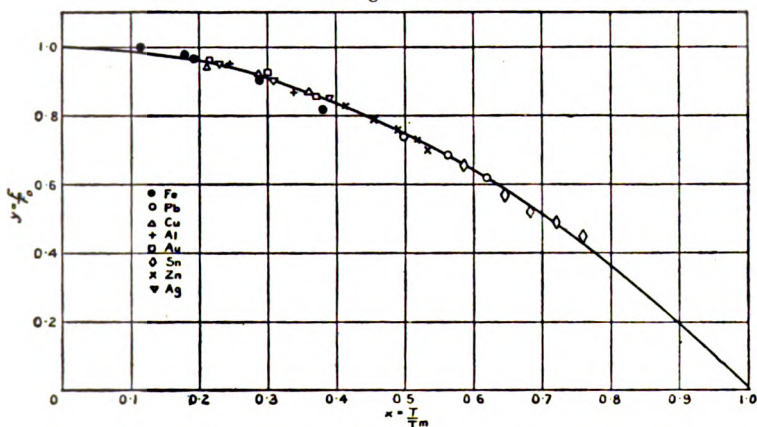


Diagram showing the Variation of the Modulus of Rigidity or Shear at various temperatures considering several different metals.

The values as shown are taken from the results published from the work of nine investigators.

$$\frac{F}{F_0} = 1 - \left( \frac{T}{T_m} \right)^2.$$

$$y = 1 - x^2.$$

Equation (7) has been used in fig. 4 in the form  $Y = 1 - X^2$ , where  $Y = \frac{F}{F_0}$  and  $X = \frac{T}{T_m}$ . The result as shown seems to

indicate very strongly that the relations for the values of the modulus of shear for varying temperatures are very well established, provided the modulus at ordinary temperatures and the melting-point of the pure metal or alloy are known.

Since the author is interested in fatigue of ferrous metals in particular, and since practically applied fatigue at high



temperatures will involve ferrous metals in the large majority of cases, the application of this relation will be carried out for ferrous metals only. It should be pointed out, however, that to apply it to any other metal requires only the appropriate substitutions in the equations and diagrams involved.

Fig. 5 shows the application of Sutherland's work to the experimental values of modulus of shear  $F$  already found for several steels. In the drawing of the curve an average value for the melting temperature of steel has been used, together with the average value obtained at the Fatigue of Metals laboratory for the modulus of shear at ordinary temperatures.

Fig. 5.

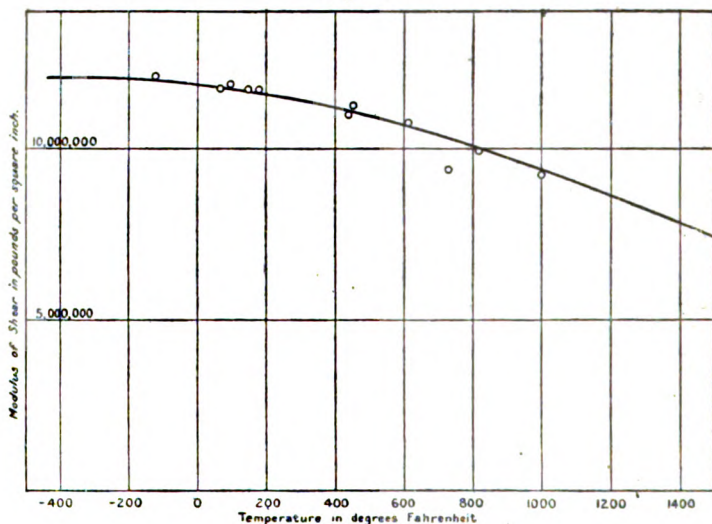


Diagram showing the variation for Steel of the Modulus of Shear or Rigidity with Temperature. The plotted values are obtained experimentally and show average results of several investigations. The results in the neighbourhood of atmospheric temperatures are the average of several determinations.

$$\frac{F}{F_0} = 1 - \left( \frac{T}{T_0} \right)^2$$

This value of the modulus of shear is the average result of measurements of about a hundred specimens comprising about twelve different steels with a range of carbon content from 0.02 to 0.93 per cent. The remainder of the plotted values on fig. 5 have been obtained from various reliable sources.

In the case of the modulus of shear for steel it is seen that in the neighbourhood of ordinary temperatures the change due to slight temperature variation may be expected to be slight. The modulus decreases progressively, however, as the temperature is increased.

The author wishes to avoid any discussion of the Kinetic Theory of Solids as presented by Sutherland, because he is not in a position to discuss it. It is desired, however, to point out that the method adopted in presenting the application of his results gives promise of being a considerable help in the solution of a rather large problem.

The theoretical relations involved between the elastic properties of an isotropic elastic material are given in the following equation :

$$E = \frac{9BF}{F+3B} \text{ and } B = \frac{FE}{9F-3E}, \quad \dots \dots (8)$$

in which B represents the bulk modulus.

For the proof of equation (8) references are made to the works of Love \*, Morley †, and others.

The bulk modulus B can be obtained from the kinetic theory of solids as referred to above. It is not thought necessary to reproduce the proof here, but it is given in detail in Sutherland's work ‡. The formula as applied is essentially as follows :

$$B = + \frac{2}{9} h \frac{Jc\delta}{\lambda} \left( \frac{1}{\lambda T} - 4 \right), \quad \dots \dots (9)$$

where

J = the mechanical equivalent of heat,

h = the specific heat of the material,

δ = the density,

λ = the coefficient of linear expansion,

c = constant for the material which is very nearly 1.

T = the temperatures absolute at which the test is to be made.

In the application of the kinetic theory of solids, Sutherland assumed average values for substitution in the above equation. It could not be expected that his experimental values would check the calculations thus found. Such coefficients as the specific heat for steel may vary one hundred per cent. between zero temperature F. and 1400° F., while the other coefficient variations by no means balance this factor.

\* A. E. H. Love, 'The Mathematical Theory of Elasticity,' 1920 edition.

† Arthur Morley, 'Strength of Materials,' 1920 edition.

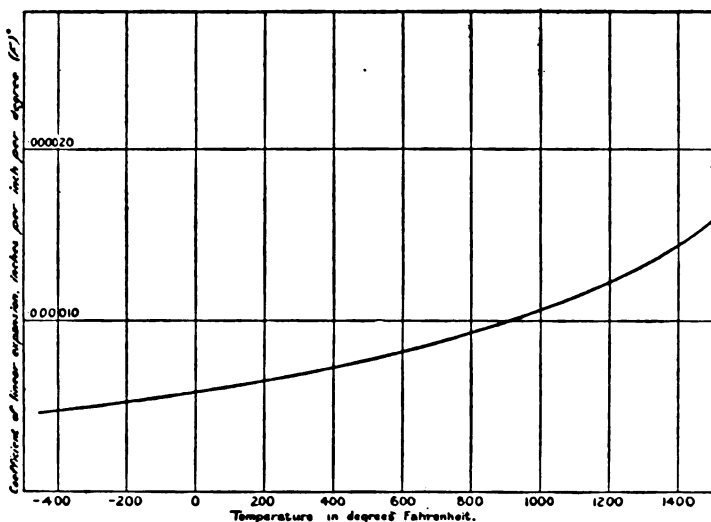
‡ "A Kinetic Theory of Solids," Phil. Mag. xxxii. pp. 524-531 (1891).

Since  $J$  and  $c$  are constants for any particular material, and  $\delta$  is so near a constant that from  $0^\circ \text{F.}$  to  $1400^\circ \text{F.}$  it will vary less than 2 per cent. for steel, equation (9) will be written in the following form :

$$B = +K_{\lambda} \left( \frac{1}{\lambda T} - 4 \right), \quad . \quad . \quad . \quad . \quad (10)$$

where  $K$  is a constant comprising all the other constant factors for steel. In fig. 6 the experimental values of the

Fig. 6.



Curve showing the Variation of the Linear Coefficient of Expansion with Temperature for Carbon Steels.

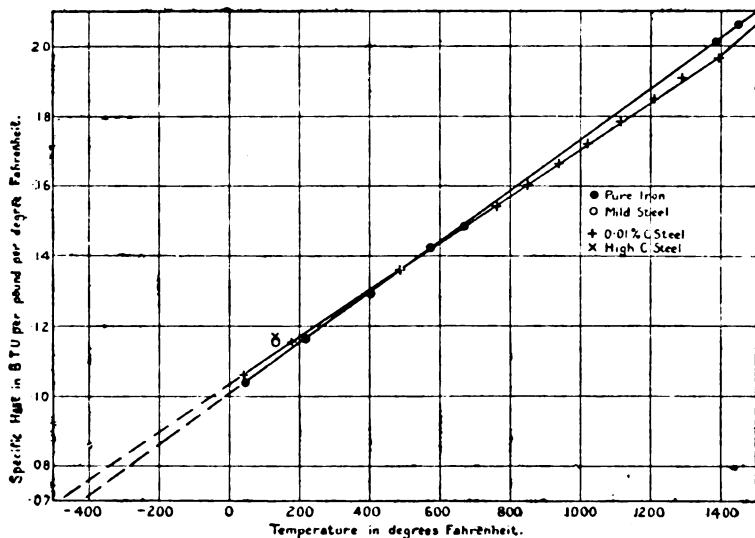
Average of seven steels.

coefficient of linear expansion for steel and in fig. 7 the specific heat of steel at various temperatures have been plotted.

From the values obtained from figs. 6 and 7 a straight substitution has been made in equation (6) for  $h$ ,  $\lambda$ , and  $T$  at ordinary atmospheric temperature. The appropriate value of the bulk modulus as obtained from experimental results on steel from the Fatigue of Metals laboratory has been used, and from substitution in equation (10) the value of  $K$  was found to be 4.1.

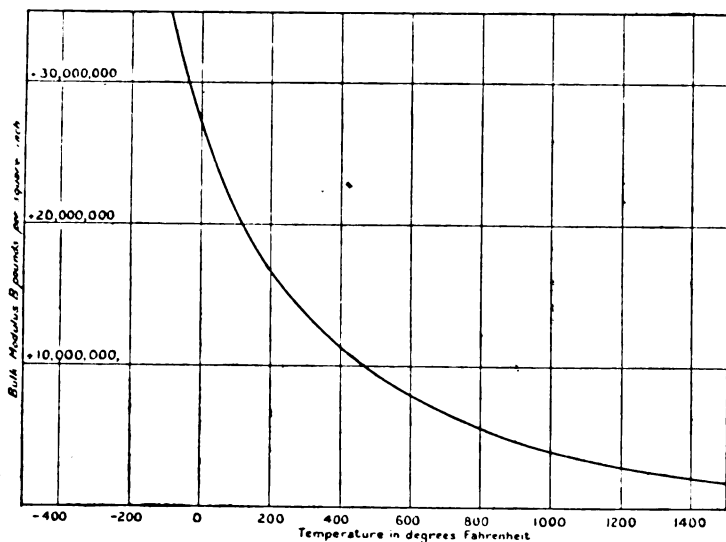
By the use of the value of  $K$  thus obtained the calculation of the bulk modulus  $B$  at various temperatures has been performed, the values being plotted in fig. 8.

Fig. 7.



Specific heat B.T.U./pound/degree F. for Steel at different temperatures. Experimental values ○, ●, ×, plotted from average values +.

Fig. 8.



Curve showing the Variation of the Bulk Modulus for Steel with Varying Temperatures.

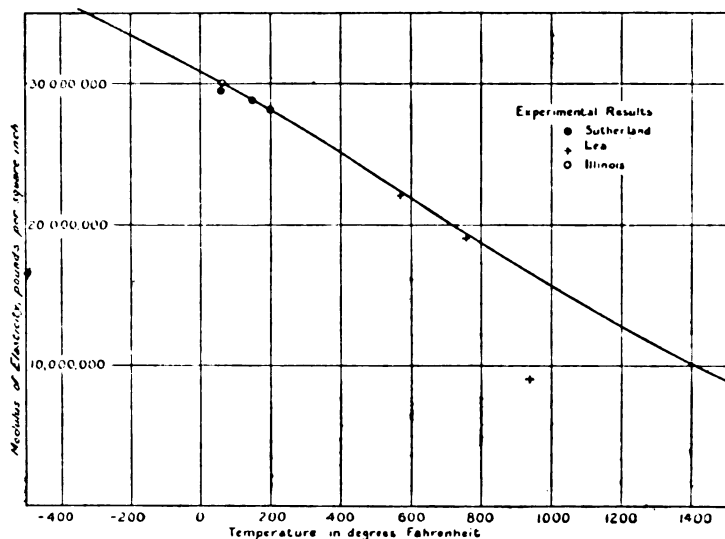
$$B = -k \lambda \left( 4 - \frac{1}{\lambda T} \right). \text{ By substitution } k = 4 \cdot 10.$$

Fig. 9 represents the value of the modulus of elasticity  $E$  obtained by substituting in the equation

$$E = \frac{3F}{1 + \frac{F}{3B}} \quad \dots \quad (8 \text{ bis})$$

the appropriate values of  $F$  and  $B$  as obtained from figs. 5 and 8.

Fig. 9.



Curve showing Variation of Modulus of Elasticity of Steel with Temperature.

$$E = \frac{3F}{1 + \frac{F}{3B}}$$

On fig. 9 have been plotted such experimental values of the modulus of elasticity  $E$  for steel at various temperatures as the author has been able to obtain.

It might be noticed that in the neighbourhood of 950° F., the experimental value of  $E$  drops off. This suggests one of two things: either the steel in the neighbourhood of this point has an abrupt change in the modulus of elasticity due to as yet an undiscovered critical point, or there is a sharp discontinuity in the factors controlling the bulk modulus of steel at this point. That the former is the case is suggested by the plotted values of the energy relation at various temperatures shown in Table I. in the latter part of this paper. The author, however, as yet has no specific evidence on this point.

*Application of the Use of the Energy Relation to Static Testing of Ferrous Materials at Various Temperatures.*

If the value of the energy required to bring a steel to its yield point, considering the elastic properties involved, can be shown to be a constant, then the energy relation can be used in such a manner as to assist the materials engineer in anticipating the strength of materials at various temperatures, and also at various ratios of ranges of stress in fatigue at various temperatures.

It is to be hoped that extensive tests in fatigue at high temperatures will be made in the near future, so that applications similar to Table I. can be made in fatigue at high temperatures for several steels. Some tests on static strength of steel have already been made by H. Brearley \*, and the energy involved in bringing such steel to the yield point will be investigated for the purpose of suggesting the use of the simple energy equation :

$$W = \frac{1}{2E} (S_1^2 + S_2^2) = \text{constant.} \quad . \quad . \quad (6 \text{ bis})$$

In the case of static testing  $S_2=0$ , and the value of the energy involved becomes

$$W = \frac{S_1^2}{2E} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Table I. shows the application of results available on the variation of the yield point at various temperatures to the equation of energy. The elastic limit values available have not been used, because the value of the elastic limit depends in large measure on the sensitiveness of the extensometer used in making the measurements, on the initial quenching strains set up in the steel tested †, and, in the case of the variation of temperature, on the relative value of the modulus of elasticity at the various temperatures. In the tests made at the University of Illinois on the fatigue strength of metals ‡, it has been found that the yield-point values are very much more significant where they are available than the elastic-limit values, and, in the case of steels which have no yield point, that the ultimate strength is the better value to use with the endurance limit as a comparator.

\* Published in Report on the Materials of Construction by the Aeronautical Research Committee, 1920, p. 37.

† Atchinson, 'Engineering Steels,' p. 114, published by Van Nostrand.

‡ H. F. Moore and T. M. Jasper, Bulletin No. 136, University of Illinois Engineering Experiment Station.

Above a temperature of 950° F., the results have not been taken as significant, because at 950° F. the experimental values of *E* have been found to be much lower than the theory indicates for steel. See fig. 9.

TABLE I.

Temperature, degrees F.	Yield point, tons per sq. in.	<i>S</i> <sub>1</sub> , lb. per sq. in.	<i>E</i> , lb. per sq. in. Calculated. Fig. 9.	$\frac{S_1^2}{2E}$	Per cent. Variation from Average Value.
65	38.8	87000	30000000	126	- 3.4
212	37.0	82800	28000000	123	- 5.7
392	37.0	82800	25300000	135	+ 3.6
572	33.44	75000	22400000	126	- 3.4
752	33.6	75300	19500000	145	+11.1
842	31.32	70300	18200000	135	+ 3.6
932	28.68	64200	16750000	123	+ 5.7
1022	22.92	51400	15500000	85	
1112	20.80	46600	13600000	80	
1292	10.84	24300	12000000	25	

*Summary.*

From the fatigue experiments carried out by Professor B. P. Haigh at the Royal Naval College, Greenwich, and at the University of Illinois by Professor H. F. Moore and the author, it would seem that the value of the energy involved per complete cycle of stress for a specific wrought ferrous metal at the endurance limit is a constant, or if used as a constant is a safe designing factor to apply, providing the yield point of the material is not exceeded.

From the experiments carried out by Mr. H. Brearley, as given in the "Report on Materials of Construction" by the Aircraft Production Department of the Ministry of Munitions, it would seem that the energy involved in bringing the stress to the static yield point for a wrought ferrous metal under different temperatures is a constant at any temperature below 950° F. Above the temperature of 950° F., it seems that the value of the modulus of elasticity changes abruptly, which suggests that there is possibly a physical critical point in wrought ferrous metals in the neighbourhood of 950° F., which has not been generally recognized up to the present time.

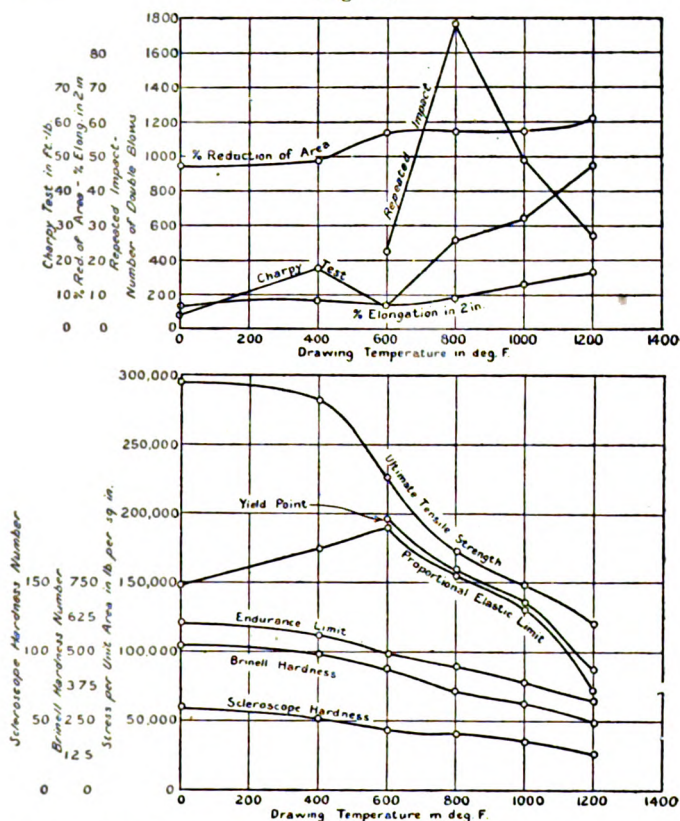
It is felt that there is a great necessity for fatigue tests at high temperatures, and it is hoped that these may be carried out in the near future. These should be coupled



with static tests to determine the static and elastic properties for various wrought ferrous metals.

It is suggested that the constant energy idea will help in determining the safe stresses to use in internal-combustion engines and heat turbines when the endurance limits in fatigue for ordinary temperatures are determined and when the static and elastic properties at ordinary temperatures are known.

Fig. 10.



Curves showing the relation between the Elastic Limit and other static properties for a Strong Steel.

It is suggested that the use of the elastic limit should be made with care, because the value obtained for this property depends in large measure on the sensitiveness of the extensometer used in determining it, on the initial quenching, rolling or forging stresses set up, and on the temperature at which the material is tested. See fig. 10.



It is suggested that if, because of the particular composition or heat treatment of a ferrous metal, the yield point cannot be determined, the most consistent static property to use is the ultimate strength with an appropriate factor.

#### APPENDIX.

As an appendix to this paper it is thought wise to refer to the respective papers of McPherran\*, Spooner†, Preston and Harder‡, which deal with the effect of temperature on the static properties of steel. No values are obtainable from these papers with reference to the elastic properties of steel, although the results referred to above are of such a character as to confirm the contention of the author of this paper, namely, that the energy relations hold as a test of strength of a material at various temperatures. The greatest complication that accrues when static results of strength are obtained at high temperatures is due to the initial state of the steel.

The application of the energy relation to static tests of heat-treated steels at high temperature is undoubtedly complicated because of the fact that a quenched steel tested at ordinary temperatures is subsequently tested at higher temperatures. A quenched steel can only, strictly speaking, be compared up to the temperature of the quenching liquid which is slightly above ordinary temperature, while a steel which is quenched from, say, 1470° F., and then drawn at 1300° F., can possibly be compared in a strict sense at higher temperatures up to 1300° F. or some critical temperature which is somewhat lower. It has been found, however, for carbon steels at ordinary temperatures that, up to a drawing temperature of about 600° F., the static and fatigue properties are very little changed with the exception of possibly the proportional elastic limit. This has been considered to be due to initial quenching strains. For steels such as nickel and chrome-nickel alloys this is not, however, the case.

It would seem that it could be contended that a quenched steel tested at ordinary temperatures and of a specific carbon content differed essentially in its static properties from the same steel tested under similar conditions, and in its annealed state. So much is this the case that to all intents and purposes it might be considered as a different material, and

\* "Comparative Tests of Steel at High Temperatures," A. S. T. M. Proc. 1921.

† "Discussion of Tests of Steel at High Temperatures," A. S. T. M. Proc. 1921.

‡ "Effect of Temperature on the Mechanical and Microscopic Properties of Steel," Chemical Engineer, Jan. 17, 1923.

certainly might be so classified if its chemical composition was not known.

It would seem, therefore, to be essential that the above phenomena should be considered in outlining tests of steel at high temperatures.

In reverting to the suggestion by the author that the papers referred to in this appendix tend to confirm the contention that the energy relations hold in strength of materials and are especially helpful in testing at high temperatures, it may be pointed out:

First, that the slopes of the stress-strain curves below the yield point vary progressively with the increase of temperature at which the material is tested, confirming the contention that the value of the modulus of elasticity decreases with increase of temperature. See fig. 9.

Second, that although in some cases the ultimate strength at 700° F. is higher than at ordinary temperatures, the per cent. reduction in area and the per cent. elongation in two inches are relatively decreased, and that in general a rapid increase or decrease of the ultimate strength is correlated with a decrease or increase in the other two properties mentioned.

Third, that in no case at a higher temperature is the yield-point strength greater than is found in the same steel at ordinary temperatures, and that in general the yield-point values decrease progressively as the temperature is increased.

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LXVIII. *The Influence of Foreign Gases on the Secondary Spectrum of Hydrogen.* By S. BARRATT, B.A. (Balliol College, Oxford) \*.

IT has long been known that the presence of foreign gases in a hydrogen vacuum tube enhances the Balmer series relatively to the secondary spectrum of hydrogen. The effect of such gases on the secondary spectrum itself was first observed by Merton (Proc. Roy. Soc. 96 A. 1920, p. 382), who found that the intensity relations among its lines were greatly changed by the presence of helium in the vacuum tube. This fact is of importance in the investigation of this complex spectrum, as it isolates a comparatively small number of lines which exhibit similar intensity changes, and which are probably related. Other methods of isolating groups of lines have recently been described (Merton and Barratt, Phil. Trans. 222 A. 1922, p. 369), and in the same paper the observations on helium were extended

\* Communicated by Prof. T. R. Merton, F.R.S.

over a wider spectrum range. At the conclusion of this work it appeared of interest to investigate whether gases other than helium affect the secondary spectrum in a similar way. With this object, experiments have now been made with argon and with oxygen.

For the experiments with argon a vacuum tube of the usual H type was constructed, and a palladium hydrogen regulator sealed into one arm. The tube was filled with argon at an estimated pressure of 15–20 mm. of mercury. The crude argon was taken from a cylinder, and was purified by passage over heated calcium. The tube was sealed, and hydrogen admitted through the regulator until the chief argon lines, such as  $\lambda 6032$ , were of about the same intensity as the secondary hydrogen lines. The spectrum from the tube was then photographed, between  $\lambda\lambda 6500$  and  $4700$ , in the first order of a concave grating which gives a dispersion of  $10 \text{ \AA. per mm.}$  A photograph of the secondary spectrum emitted by a tube filled with pure hydrogen was taken with the same setting of the instrument, and the two plates compared in juxtaposition under a travelling microscope.

It was found that argon does alter the distribution of intensity in the secondary spectrum, but that the effect is much smaller than that produced by the same pressure of helium. A list of the relatively enhanced lines is given at the end of the paper. It will be seen that most of the affected lines are also enhanced by helium, but there are several exceptions. On the other hand, many lines included in this wave-length range and markedly enhanced by helium are quite unaffected by argon.  $\lambda 6392.99$  and  $\lambda 6111.08$ , two of the secondary hydrogen lines previously only observed in the presence of helium, proved to be developed also with argon. No lines were found to be enhanced of shorter wave-length than  $\lambda 5667$ , and the investigation was not extended below  $\lambda 4700$ , as helium itself exerts very little influence beyond this region.

The effect of oxygen was studied by an examination of the spectrum given by water vapour. A vacuum tube was prepared with a side tube containing small lumps of potash. The tube was evacuated as far as possible by a Gaede pump, and then sealed. By warming the potash, a pressure of water vapour could be liberated suitable for the purpose in view; and the potash also served as a trap for the traces of carbon gases with which a freshly prepared vacuum tube is commonly contaminated, even after careful preliminary exhaustion. In the spectrum of a tube filled with water vapour the Balmer series are strongly developed, while

the secondary hydrogen spectrum is bright enough to be photographed, though weaker than in pure hydrogen. A photograph of the spectrum was secured, as with the argon tube, and over the same wave-length range. This was compared with a plate of suitable intensity taken with pure hydrogen. Apart from a doubtful, and in any case slight, enhancement of the Fulcher bands, the secondary spectrum proved to be identical on the two plates, showing that the intensity distribution in this spectrum is unaltered by the presence of oxygen.

It must be concluded from these experiments that the great intensity changes in the secondary hydrogen spectrum produced by the presence of helium are not reproduced by other gases. Changes evidently related, though on a far smaller scale, are produced by argon, a member of the same periodic group, while oxygen exerts no influence of the kind.

TABLE of Lines in the Secondary Spectrum of Hydrogen relatively enhanced by the presence of Argon.

$\lambda$ .	Effect of argon.	Effect of helium.
6495.78 ....	+	+
6487.76 ....	+	
6392.99 ....	++	++
6279.85 ....	+	
6264.89 ....	+	
6219.40 ....	+	
6193.80 ....	++	+
6186.52 ....	+	+
6181.44 ....	+	+
6179.19 ....	+	
6141.79 ....	+	
6140.97 ...	++	++
6119.00 ....	++	+
6112.80 ....	+	+
6111.08 ....	++	++
6085.20 .....	++	++
6058.28 ....	++	++
6056.10 ....	+	++
6006.91 ....	+	++
5998.02 ....	+	+
5847.29 ....	++	++
5672.73 ....	+	++
5667.40 ....	+	++

The wave-lengths are those given by Merton and Barratt (*loc. cit.*), and the data for the effect of helium on the lines are taken from the paper by Merton already quoted. The system of crosses indicates the degree of enhancement, a double cross indicating a greater degree than a single cross.

LXIX. *The Motion of Electrons in Carbon Monoxide, Nitrous Oxide, and Nitric Oxide.* By M. F. SKINKER, M.Sc., *Exeter College, Oxford*, and J. V. WHITE, B.A., *Exeter College, Oxford* \*.

1. **I**N the November number of the Philosophical Magazine an account was given of the motion of electrons in carbon dioxide. In this paper we wish to give the results of similar experiments with carbon monoxide, nitrous oxide, and nitric oxide.

The experimental part of the investigation consists principally in measuring the velocity  $W$  of the electrons in the direction of the electric force and the velocity of agitation  $u$  corresponding to various electric forces  $Z$  and gas-pressures  $p$ . The apparatus used in all these experiments was the same one which was used in the experiments with  $\text{CO}_2$ , and the method of making the measurements has already been fully described †.

2. From theoretical considerations it may be seen that the velocities of electrons  $u$  and  $W$  are functions of the ratio  $Z/p$ , and several experiments have been made with different forces and pressures in order to test these results. But when electrons tend to form ions by adhering to molecules of the gas, the proportion of the number of ions to the number of electrons increases with the pressure in an apparatus of fixed dimensions, and the values of  $u$  and  $W$  for a stream containing ions and electrons as found experimentally diminish as the pressure increases. Within the range of forces and pressures used in the determinations of the motion of electrons in carbon dioxide, and in the determinations made by Prof. Townsend and Mr. Bailey ‡ of the motion of electrons in oxygen, nitrogen, hydrogen, and argon, it was found that in nitrogen, hydrogen, argon, and carbon dioxide the velocities  $W$  and  $u$  were functions of the ratio  $Z/p$ , but in the case of oxygen the values of  $W$  and  $u$  corresponding to the larger pressures were smaller than those corresponding to the smaller pressures when the ratio  $Z/p$  was maintained constant. This effect is most marked with the smaller values of the ratio  $Z/p$ .

\* Communicated by Prof. J. S. Townsend, F.R.S.

† M. F. Skinner, *Phil. Mag.* vol. xlv. Nov. 1922.

‡ *Phil. Mag.* vol. xlii. Dec. 1921, and vol. xliii. March 1922.

Thus the gases may be divided into two classes—those like nitrogen, hydrogen, argon, and carbon dioxide, where there is no tendency for the electrons to form ions and the velocities are functions of the ratio  $Z/p$ ; and those like oxygen, where ions may be formed and the velocities, as found experimentally for a given value of the ratio  $Z/p$ , diminish as  $p$  increases.

We have found that in carbon monoxide, as in carbon dioxide, the electrons do not tend to form ions, but in nitric oxide ions are formed, and, as in the case of oxygen, this effect is most noticeable with the smaller values of the ratio  $Z/p$ . With nitrous oxide a different result was obtained. In this case, for the smaller values of the ratio  $Z/p$  the velocities are, within experimental error, functions of the ratio  $Z/p$ , and by a direct method of testing for the presence of ions it was found that there were very few ions in the stream. For the larger values of the ratio  $Z/p$  the velocities are not functions of this ratio, and by the direct method of testing it was found that there were a large number of ions in the stream.

3. The direct test for the presence of ions in the stream of electrons passing through a gas is made by observing the effect of the magnetic field on the charges acquired by the receiving electrodes. The values of  $W$  were calculated by deflecting the centre of the stream with a magnetic field through an angle whose tangent is  $1/6$ . If the stream consisted only of free electrons, then a magnetic field of from five to ten times as large would deflect the entire stream through this angle. This field, however, would not be sufficient to deflect particles of ionic mass by an appreciable amount. Therefore, if an undeflected portion could be detected under these conditions, it would show that ions were present in the gas.

We have found that in carbon monoxide the stream was free from ions, as it also was in carbon dioxide, nitrogen, hydrogen, and argon. With nitric oxide and nitrous oxide a small proportion of the stream could not be deflected through the small angle  $\tan^{-1} 1/6$  with a current of twenty times that used in determining  $W$ .

4. In Table I. the results of the experiments with carbon monoxide are given, and it will be noticed that there is good agreement between the values of  $k$  and  $W$  for each value of the ratio  $Z/p$  obtained with different forces and pressures. In this gas, within the ranges of forces and pressures given in the table no indication of ions was found by the direct method of testing.

TABLE I.  
Carbon Monoxide—CO.

$p$ .	$Z$ .	$Z/p$ .	$k$ .	$W \times 10^{-5}$ .
40	4.28	107	1.89	6.45
20	2.14		1.91	6.59
20	4.28	214	3.04	8.80
10	2.14		3.12	8.63
20	8.56	428	4.68	11.60
10	4.28		4.57	12.00
5	2.14		4.66	12.10
20	17.12	856	6.36	16.00
10	8.56		6.48	16.10
5	4.28		6.37	16.20
2.5	2.14		6.48	16.60
20	34.24	1.71	10.12	21.30
10	17.12		10.08	22.00
5	8.56		9.95	22.60
2.5	4.28		10.19	22.60
1.25	2.14		10.05	22.80
10	34.24	3.42	17.47	26.30
5	17.12		17.92	26.60
2.5	8.56		17.50	26.40
1.25	4.28		17.24	26.70
5	34.24	6.85	28.30	32.00
2.5	17.12		28.25	32.00
1.25	8.56		28.45	32.20
2.5	34.24	13.70	37.20	46.40
1.25	17.12		38.70	44.80
.625	8.56		38.60	45.90
1.25	34.24	27.39	48.60	72.70
.625	17.12		47.80	71.80
.625	34.24	54.78	90.00	145.00
.3125	17.12		94.00	143.00

In Table II. the results of the experiments with nitric oxide are given, and in this case it is seen that, for each value of  $Z/p$ , the velocities diminish as  $Z$  and  $p$  increase in the same proportion. With this gas the presence of a small number of ions was detected by the direct method.

The comparison between the values of  $W$  and  $k$  for these gases and the values of nitrogen are shown by means of the curves. Figs. 3 and 4 show the values of  $W$  and  $k$  respectively plotted against values of  $Z/p$ , and in figs. 1 and 2 the first parts of these curves are plotted on a larger scale.

TABLE II.  
Nitric Oxide—NO.

$p$ .	$Z$ .	$Z/p$ .	$k$ .	$W \times 10^{-5}$ .
10	4.36	.44	2.89	9.92
5	2.18		4.03	18.80
10	8.72	.87	6.12	14.5
5	4.36		6.51	21.8
2.5	2.18		6.60	29.2
10	17.44	1.74	7.44	23.4
5	8.72		8.55	30.2
2.5	4.36		9.50	32.1
10	34.88	3.49	10.69	37.6
5	17.44		11.80	42.9
2.5	8.72		12.20	42.5
1.25	4.36		12.50	42.1
5	34.88	6.98	14.85	61.4
2.5	17.44		15.40	62.6
1.25	8.72		15.70	66.8
2.5	34.88	13.95	41.6	84.9
1.25	17.44		44.1	88.8

Fig. 1.

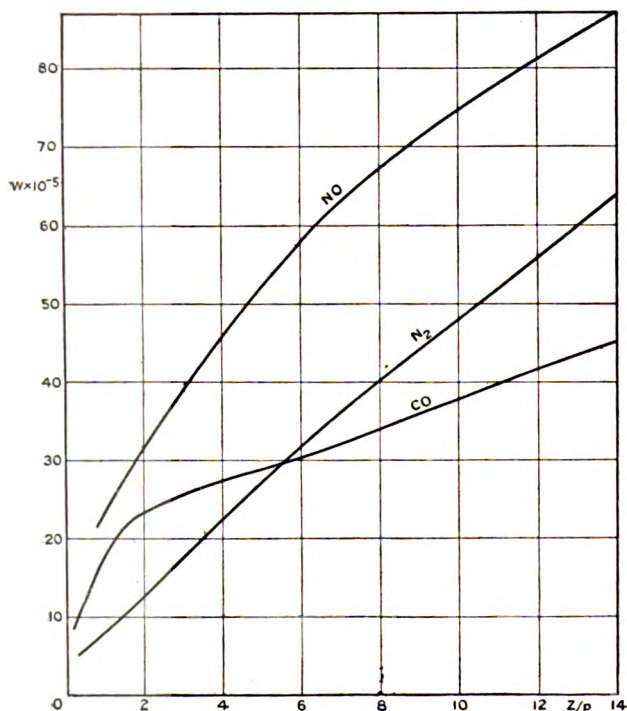




Fig. 2.

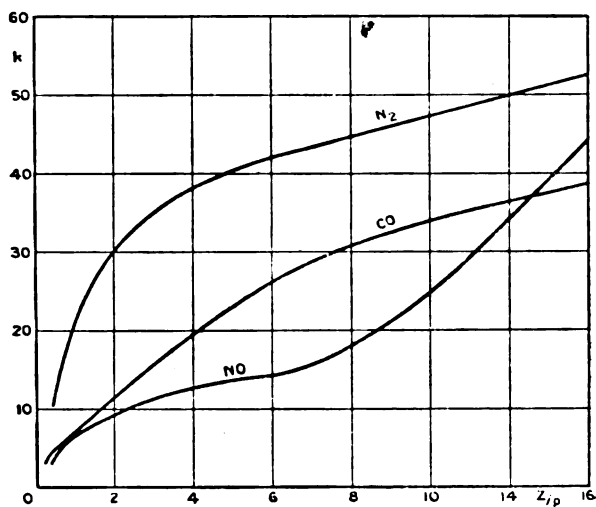
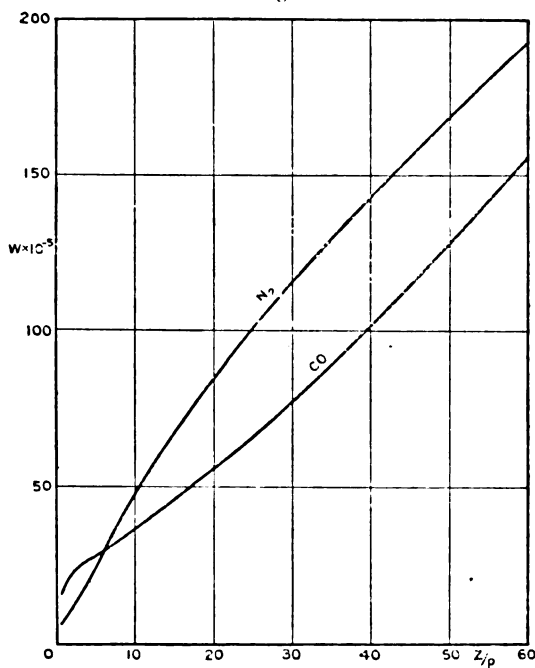
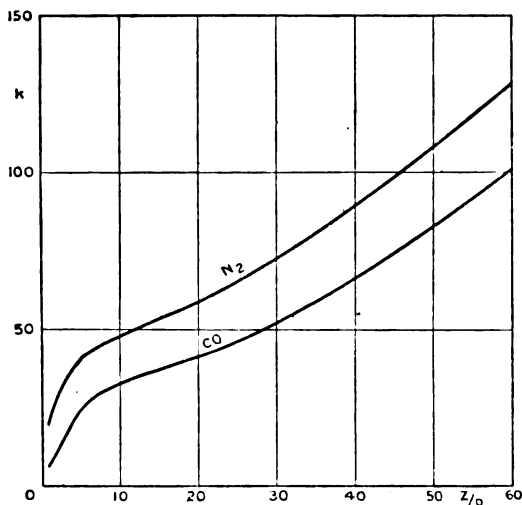


Fig. 3.



Considerable difficulty was found with the nitrous oxide, as it changed slightly after it had been experimented upon, especially at the higher electric forces  $Z$ . But by using fresh quantities of gas in the apparatus consistent results were obtained. Two methods of preparation of the gas were

Fig. 4.



used, and identical results were obtained. In the first section of Table III. the agreement of  $k$  and  $W$  is good for the same values of the ratio  $Z/p$ , but in the second section there are a great many ions in the stream, probably due to the decomposition of the gas under these conditions.

5. The values of the mean free path  $l$  of the electrons in centimetres, the effective radius  $\sigma$  of the molecules of the gas in centimetres, and the proportion  $\lambda$  of the energy lost in collision with a molecule are given by Tables IV. and V. for carbon monoxide and nitric oxide.

The quantities  $\sigma_1$  at the top of the tables are the values of the radii obtained by the viscosity method\*.

In the values of  $\lambda$  for the carbon monoxide there is a maximum when  $k$  is equal to 5.5. Also in the carbon dioxide there was a similar maximum when  $k$  was equal to 20.

\* Jeans, 'Dynamical Theory of Gases,' p. 327 (1921).

TABLE III.  
Nitrous Oxide— $\text{N}_2\text{O}$ .

	$p$ .	$Z$ .	$Z/p$ .	$k$ .	$W \times 10^{-5}$ .
1 ...	10	4.17	.42	1.32	7.31
	5	2.08		1.32	7.66
	10	8.33	.83	—	16.10
	5	4.17		1.81	16.40
	5	8.33	1.66	2.69	32
	2.5	4.17		2.71	32
	5	16.67	3.33	4.65	42.5
	2.5	8.33		4.99	49
2 ...	1.25	4.17		5.28	48
	2.5	16.67	6.66	8.05	46
	1.25	8.33		9.07	50
	.625	4.17		10.50	50
	1.25	16.67	13.33	12.40	46.5
	.625	8.33		15.15	49

TABLE IV.  
Carbon Monoxide— $\text{CO}$ .

$$\sigma_1 = 1.90 \times 10^{-8}.$$

$Z/p$ .	$k$ .	$W \times 10^{-5}$ .	$u \times 10^{-6}$ .	$lp \times 100$ .	$\sigma \times 10^8$ .	$\lambda \times 10^4$ .
50	86	152	106.7	2.24	2.02	499.0
40	68	114	94.6	1.87	2.22	357.0
30	52	80	83.0	1.53	2.45	228.5
20	42	57	74.5	1.47	2.50	144.0
10	34	38	67.0	1.76	2.29	79.1
5	22.7	28.5	54.8	2.16	2.06	52.8
3	16	26	46.0	2.76	1.83	78.6
2	11	23	38.2	3.04	1.74	89.1
1	5.5	18	27.0	3.36	1.66	109.3
.5	4.8	13	25.2	4.52	1.43	65.5
.25	3.2	9	20.6	5.14	1.34	46.9

The energy of agitation of the electrons is proportional to  $k$ , and may be expressed in terms of the potential required to impart an equal quantity of energy to a particle having an atomic charge. This potential in volts is  $k/27$ . Thus

electrons lose a large proportion of their energy when they collide with molecules of carbon monoxide with velocities corresponding to .2 volt, and of carbon dioxide with velocities of .74 volt.

TABLE V.  
Nitric Oxide—NO.

$$\sigma_1 = 1.88 \times 10^{-8}.$$

$Z/p.$	$k.$	$W \times 10^{-5}.$	$u \times 10^{-6}.$	$lp \times 100.$	$\sigma \times 10^8.$	$\lambda \times 10^4.$
13	37.0	38.0	70.0	1.42	2.55	74.3
10	21.7	23.6	53.6	.88	3.24	47.7
8	16.7	18.0	47.0	.73	3.54	36.1
5	13.3	14.5	41.9	.84	3.31	29.4
4	12.2	13.9	40.2	.97	3.10	29.5
3	11.0	12.5	38.2	1.10	2.89	26.4
2	9.3	10.0	35.1	1.21	2.75	20.0
1	7.0	6.5	30.4	1.37	2.59	11.2

*Note.*—In a previous paper by Prof. Townsend and Mr. Bailey \* some cases were mentioned where there is a comparatively large loss of energy when electrons collide with molecules, and it was implied that in all such cases there are ions in the gas—for example, in carbon dioxide. The statement was based upon the fact that  $k$  was found to be small in some of the earlier experiments with this gas, and the value of  $k$  for ions must be approximately unity. Large values of  $k$  can only be obtained with electrons, but the recent experiments with carbon dioxide †, where both  $k$  and  $W$  were measured, show that  $k$  may be very small for a stream of electrons. In this gas the velocity  $W$  is very large, even when  $Z/p$  is small, due to the fact that the electrons lose a large proportion of their energy in collision, but do not form ions.

\* Phil. Mag. vol. xlii. Dec. 1921, p. 891.

† M. F. Skinner, Phil. Mag. vol. xlv. Nov. 1922.

**LXX. On Types of Crystal Symmetry in which no finite symmetrical crystal unit having the complete symmetry of the crystal is to be found.** By WILLIAM BARLOW, F.R.S.\*

**T**HE geometrical study of crystal structure is based on the law of rational indices as exemplified by the variety of forms of crystal symmetry presented in nature. Some 30 years ago, 230 distinct types of homogeneous structure were discriminated according to one or other of which alone the parts of a given individual homogeneous crystal must be regarded as arranged †.

Every similar unsymmetrical space-unit of the space-filling uniform partitioning of a given individual crystal is by every coincidence operation characteristic of the particular type of the 230 concerned transferred to an entirely distinct position; the original and derived positions show no overlapping whatever.

For the purpose of visualizing this condition of things for some of the more regular types of the 230, the writer constructed models in which similar dolls' hands were placed in an open framework in relative positions located by the characteristic coincidence operations of one or other of these types ‡.

In order to derive some partitioning of space appropriate to an individual case of any given type, every doll's hand in the appropriate artificial structure can be supposed to grow similarly, and to cease growing wherever and so soon as the moving boundaries come in contact with one another. Space is in this way conceived to be partitioned without leaving interstices into similar grotesque cells presenting in nearly all cases more than one orientation. All of these cells are capable of being brought to coincidence one with another by some appropriate coincidence movement or mirror-image operation characteristic of the type of the 230 in question. In cases of types presenting a mirror-image relationship of some kind, two sets of dolls' hands are employed, rights and lefts equally numerous and similarly distributed.

It is obvious that the space-unit of this conception is destitute of symmetry.

\* Communicated by the Author.

† Groth's *Zeitschr. für Kryst.* xxiii. p. 1, xxv. p. 86. "Report on the Structure of Crystals," Brit. Assoc. Glasgow, 1901.

‡ He exhibited these models at a Royal Society soirée and elsewhere in this country; also on the Continent. They are now in the Natural History Museum at South Kensington.

The important question arises:—Is there any evidence of the universal presence of units of any nature, space-units or other, which epitomize the crystal symmetry?

It is clear that there is no geometrical necessity for the presence of such a representative symmetrical unit; the crystal symmetry is completely developed by the characteristic symmetrical operations of the type of crystal symmetry concerned as applied to a quite unsymmetrical unit. It may, however, be asked:—Is it not possible that while the space allotted to the crystal unit is unsymmetrical, this unit somehow presents or constitutes part of a form which is an epitome of the crystal symmetry concerned?

There is a serious objection to this suggestion. No crystal symmetries are known which are not comprised in those of the 230 types referred to. Other symmetries equally high but quite distinct from these are found in organic nature—*e. g.*, the five-fold symmetry occurring in some vegetable and animal structures. Why does no crystal present a symmetry outside the 230 types; for example, one corresponding to the completely symmetrical pentagonal dodecahedron? If the crystal unit is in all cases a perfect epitome of the crystal structure, what essential limitation is it which excludes this and all other highly-symmetrical types of symmetry which are not such as are completely developed by the coincidence operations of one or other of the 230 types?

Again: If, for argument's sake, the possibility of the unit in all cases possessing a symmetry which is an epitome of the crystal symmetry is accepted, there is another fundamental difficulty.

A large majority of the 230 types admitted to be geometrically possible for crystals will in this event owe their symmetry entirely to the form of the unit and not even partially to the relative situation of two or more units. This will apply to all types in which any one of the minimum group of coincidence operations is a screw-movement.

For the relation between the individual space-units of an infinite linear series, the presence of which series is indicated by the existence of a screw-movement connecting the units, is in no case consistent with any aggregation of units thus connected being finite; a selection of two or more units to form a finite group is quite arbitrary. Nearly three-fourths of the 230 types are affected.

A word as to the residue of the 230 types in which the existence of a composite finite group formed of several units is not precluded.

These composite similar groups will be regarded as fin

symmetrically-constituted aggregates of units, which latter, taken alone, may be either unsymmetrical or possessed of a symmetry equal to or greater than that presented by the crystalline mass. This is manifestly in harmony with the view that in the majority of cases the homogeneous crystal structure owes its symmetry to the symmetrical disposition, and not to the symmetrical form of identical units of which it is composed.

The author may remark that owing to some misconception his previous work has been cited as supporting the idea that every crystal is built up by the repetition throughout its volume of a certain unit which as to its symmetry is a perfect epitome of that of the whole\*. A perusal of his contributions to the 'Mineralogical Magazine' and to Groth's *Zeitschrift*, published in the 'nineties, will show that then, as now, he held the contrary to be proved.

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LXXI. *A Note on Dr. Hartridge's Paper on Visual Acuity.*  
By Instructor-Commander T. Y. BAKER, R.N., Admiralty  
Research Laboratory, Teddington †.

IN a paper by Dr. H. Hartridge on "Physiological Limits to the Accuracy of Visual Observation and Measurement" (Phil. Mag. No. 271, July 1923) Section IV. is devoted to Interpolation Methods of Measurement. The section deals with the ability of the eye to estimate the proportionate position of a datum mark between two successive divisions of a scale, and the conclusions reached by the author are that there is considerable inaccuracy in making this type of measurement. His conclusions seem to be based upon an attempt to subdivide a millimetre into tenths when placed at a distance of 25 cm. from the eye.

It appears to me that a single test of this description is inadequate, and that Dr. Hartridge has not given the eye sufficient credit for its power to make an accurate interpolation. He has dealt with one case only—a case in which the division to be subdivided subtends an angle of less than a quarter of a degree at the eye. Without question the magnitude of that subtended angle is of importance. If it is too small and if it is too large, accuracy of interpolation is bound to suffer, and there must be some optimum angle for which interpolation acuity reaches its maximum. Some time

\* Transactions Chemical Society, vol. cxxi. p. 2766 (1922).

† Communicated by the Author.

ago I made some rough experiments on this point, but unfortunately the results were not published, and I am unable at the present moment to lay my hands upon them, but to the best of my recollection acuity is greatest when the division subtends at the eye an angle of about three degrees. If Dr. Hartridge had carried out his test as an attempt to subdivide a centimetre placed at the near point of vision, I think he would have found that the eye would make a much better showing than his Table III. exhibits. For example, in his attempt to place the datum mark one-tenth of the distance from one end his error is so great that the position is very nearly one-fifth. Errors of a similar character, but less pronounced in value, occur at other places.

As against these poor results, I found that, provided the whole division appears of suitable size to the eye—and in an actual measuring instrument this can always be secured by a reading microscope of adequate power,—a moderately skilled observer will always read by estimation the position of the datum mark accurately to one-fiftieth of a division. A highly-skilled observer will do better than this, and I understand that at the National Physical Laboratory there are a number of persons who habitually subdivide by estimation accurately to a one-hundredth part. Reading and setting are not quite the same thing, and possibly not quite so high an acuity can be reached with the latter operation as with the former.

A deduction can be made from the above facts that is of great importance in the proper design of instruments of measurement. It is that it is unnecessary to employ a vernier if it is not required to subdivide a scale-division below one-fiftieth part. The eye can estimate with sufficient accuracy, provided a suitable optical magnification is fitted so as to make the angular value of the scale-division at the eye about three degrees. Yet how commonly does one see a vernier fitted for the purpose of subdivision very much coarser than this. Verniers to read twentieths or tenths are frequently found. I have even seen a barometer that had a vernier to read fifths!

It may also be of interest to readers of Dr. Hartridge's paper to add a short note on the acuity of the eye on separating two bright points.

I have recently had under construction at the Admiralty Research Laboratory a prismatic astrolabe, to be used for determination of latitude and longitude in geodetic survey.

*Phil. Mag. S. 6. Vol. 46. No. 274. Oct. 1923.* 2 T



The instrument is used by noting the instant of contact in the field of view of a telescope of two images of a star, one of which moves downwards and the other upwards. The acuity of the eye is rather better in noticing this instant of contact than in resolving a double star, but is not so good as we required. We got over the difficulty by placing across a part of the light that went to form one star image a small refracting prism, and thereby produced a double image in place of the single one. The prism was so arranged that the duplicate images were in a horizontal line, and had an angular separation at the eye of about half a degree. The instant of contact was then noted by observing when the single image moving downwards passed between and was in line with the double image moving upwards. A laboratory trial of about five hundred observations gave a mean error at the eye of about 12" for one observer and 18" for another. These errors are only about one-third as great as when two single images are used.

LXXII. *Radio-active Disintegration Series and the Relation of Actinium to Uranium* \*. By A. S. RUSSELL, M.A., D.Sc., Student and Tutor of Christ Church, Oxford †.

§1. *Introduction.*

THE object of this paper is to inquire how far existing data relating to the members of the three known disintegration series throw light on the subject as a whole, and particularly on the relation of the actinium to the uranium series. The writer has been able to deduce that there are probably four independent disintegration series, and to give the path of disintegration of each of them; to conclude that actinium arises probably from an isotope of uranium of atomic weight 239; to establish rough empirical relations between the periods of known radio-elements and to predict those of undiscovered ones, and to suggest the possibility of new end-products. He is aware of the difficulty of generalizing or in making deductions from the few facts there are relating to the disintegration series. The success of the Geiger-Nuttall relation, however, and of the Group-Displacement law, and the help afforded by empirical

\* A preliminary account of part of this work appeared in 'Nature,' vol. cxi. p. 703 (1923).

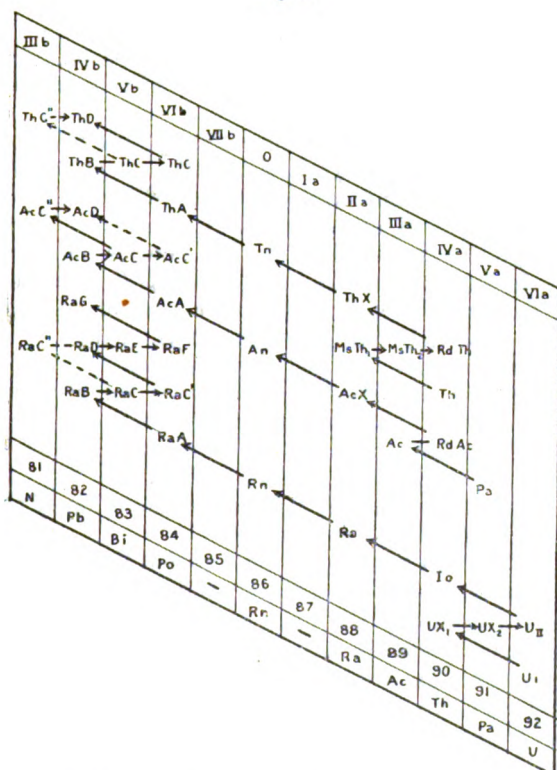
† Communicated by the Author.

relations like the  $\alpha$ -ray and  $\beta$ -ray rules of Fajans have shown that deductions of this class are not without their uses.

§2. *Deductions from Analogies in the three Disintegration Series.*

In fig. 1 are set out the three disintegration series in the usual form,  $\alpha$ -changes being represented by the upwards-sloping arrows,  $\beta$ -changes by horizontal arrows. The nomenclature is that of the International Table for 1923.

Fig. 1.



The figure omits the branch-products of uranium  $X_1$  and the bodies which precede proto-actinium in its series, but, otherwise, it represents the whole of the radio-elements known with certainty at the present time.

The following facts, obvious from the diagram, will be made use of in what follows, and will for convenience be

referred to as Rules ( $z$  is used for atomic number,  $a$  for atomic weight) :—

I. A series commences with the expulsion of an  $\alpha$ -particle followed by one or two  $\beta$ -particles, and does not end immediately after a succession of  $\alpha$ -particles.

II. No bodies of atomic numbers 93, 87, or 85 appear to exist. Corollaries of this are that bodies of  $z=92$  and  $z=84$  expel  $\alpha$ -particles only, and those of  $z=89$   $\beta$ -particles only.

III. There are only three types of successive disintegration at present known :

- (a) A succession of at least 4  $\alpha$ -particles without the expulsion of separate  $\beta$ -particles. This will be called a  $\Sigma\alpha$  change.
- (b) An  $\alpha$ -particle followed by two  $\beta$ -particles in succession and then an  $\alpha$ -particle. This will be called a  $\beta_1$  change.
- (c) An  $\alpha$ -particle followed successively by a  $\beta$ -, an  $\alpha$ -, and a  $\beta$ -particle, or a  $\beta$ -particle followed successively by an  $\alpha$ -, a  $\beta$ -, and an  $\alpha$ -particle. Either of these will be called a  $\beta_2$  change.

A change like that of RaA to RaG consisting of two  $\beta_1$  changes in succession will be called a  $\beta_1\beta_1$  change; a  $\beta_1$  change followed by a  $\beta_2$ , *i.e.*, in succession an  $\alpha$ -,  $\beta$ -,  $\beta$ -,  $\alpha$ -,  $\beta$ -,  $\alpha$ -,  $\beta$ -particle will be called a  $\beta_1\beta_2$  change.

The following is deduced from a consideration of the atomic weights of radio-active isotopes on any accepted theory of the origin of the actinium series :—

IV. The maximum difference between the atomic weights of members of any group of isotopes is 8.

The following is deduced from a consideration of the half-value periods of radio-elements :—

V. In  $\beta_1$  and in  $\beta_2$  changes the period of the first  $\beta$ -particle body is greater than that of the second.

Finally, to simplify the discussion the following limiting assumptions are made :—

VI. (a) The atomic weights of isotopes obey Aston's whole-number rule; (b) When branching occurs interest is confined to the main series; (c)  $\alpha$ - and  $\beta$ -particles are the only particles expelled in a radio-active change.

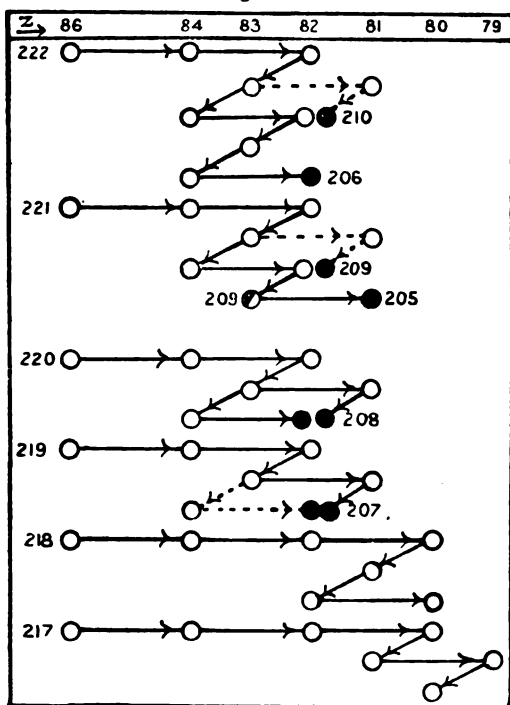
### §3. *Possible Independent Disintegration Series.*

For convenience the disintegration series will be named after the number equal to the atomic weight of the  $z=86$  member, 222 and 220 representing the uranium and thorium series respectively. The sequence of changes occurring in

these and other hypothetical series *after* the emanation will first be considered, and later those occurring *before* the emanation.

(a) *Changes after the Emanation.*—These are shown in fig. 2 for series 222, 221, 220, 219, 218, and 217, the paths of disintegration of series 221, 219, 218, and 217 being deduced from those of 222 and 220 by symmetry. Other series have not been included because their existence is

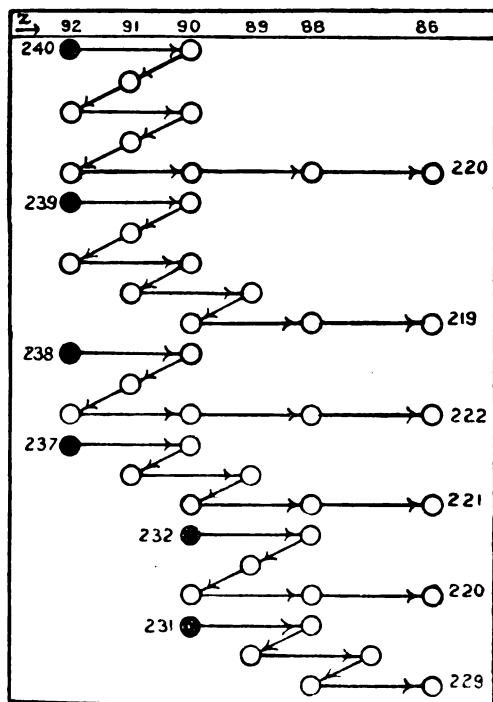
Fig. 2.



rendered improbable from the statements of §2. It is not likely that series 223, 224, etc., exist. If such did, their  $z=84$  members would have atomic weights  $a=219, 220$ , etc., which exceed by more than 8 units the atomic weight of polonium ( $z=84, a=210$ ). These series might, however, avoid passing to  $z=84$  directly, *i.e.*, the  $z=86$  member might emit  $\beta$ -particles, but at present this appears unlikely. There is no such objection to the hypothetical series 221 and 219. They should pass from their  $z=84$  to their  $z=82$  members by changes  $\beta_1\beta_2$  and  $\beta_2$  respectively, as shown in fig. 2. Series 217 is not unlikely, but 218 is. The latter

would be expected by analogy to pass from its  $z=82$  to its  $z=80$  member by a  $\beta_1$  change, the former by a  $\beta_2$  change. As the isotopes of  $z=79, 80, 81$ , and  $82$  are inactive isotopes it is reasonable to expect that such changes might occur. One of the  $z=80$  members of series 218, however, would have an atomic weight of 206, which by Rule IV. renders its existence improbable since the lightest isotope of mercury, according to Aston, has  $a=197$ . There is no objection to series 217 on this ground.

Fig. 3.



(b) *Changes before the Emanation.*—Suppose next that a similar set of changes, as are assumed to occur after the emanation members of series, occur at the beginning. These are shown in fig. 3. The atomic weights of the first members of the 3rd and 5th of these are known (being 238 for uranium I and 232 for thorium); in consequence those of the first members of the series as arranged are in order 240, 239, 238, 237, 232, and 231. Rule IV. renders improbable

the existence of series that start on atomic weights greater than 240 or less than 231. It follows that possible series are limited to those shown, and are as numbered in the figure.

It is seen that there are two possible 220 series and two 219. The first 220 series is improbable because it would contain a body  $z=90, a=236$ , which has an atomic weight 9 units greater than  $z=90, a=227$ , which will later be shown to be radio-actinium. The second 219 series is improbable because its  $\beta_2$  change contravenes Rule II. Series of lower number than 219 appear improbable because their existence would contravene either Rule II. or Rule IV.

It thus appears likely from these simple analogies and reasonable assumptions that there are only four complete radio-active series of the type that is known, namely 222, 221, 220, and 219. The path of disintegration of each of these appears from the analysis to be unique. 221 is a new series which will be sought for. Branching in the upper parts of the series is, however, not thereby excluded, because the branchings known to occur in the lower parts have not been considered. This point and empirical relations connecting branching factors will be discussed in a subsequent paper.

#### §4. *The Relation of Actinium to Uranium.*

In this section it will be shown that series 219 is the actinium series. The lower part of 219 is obviously that of the actinium series, and this fact, with the assumption that *the type of  $\beta$ -ray change is a simple function of the atomic weight*, establishes the point. Another argument in favour of this will be given later, but before that is done a short account of the rival views with respect to the origin of actinium will be given.

Boltwood \* was the first to establish quantitatively a connexion between the actinium and uranium series by showing (a) that in old, unweathered uranium minerals the ratio of the activities of uranium and actinium was constant, and (b) that no actinium was present in thorium minerals. This result was at first interpreted as proving that the actinium series necessarily arose as a branch series, and the branching was believed to occur most probably either at uranium II or uranium I. This is still the most favoured view †. It is thought that the dual change occurs at uranium II, about 97 per cent. of atoms forming ionium and the radium series,

\* B. B. Boltwood, *Phys. Review*, vol. xxii. p. 320 (1906).

† It is that given in the works on Radio-activity of Rutherford, Soddy, Meyer & Hess, Fajans, Russell, v. Hevesy & Paneth.

and the remainder forming uranium Y, the product of which, proto-actinium, is the parent of the actinium series. On this view the atomic weight of actinium is 226.

Fajans, from a general consideration of his  $\alpha$ -ray and  $\beta$ -ray rule, first suggested the possibility of actinium's atomic weight being 227. In 1917 Piccard\*, from a consideration of the Geiger-Nuttall relation, put forward the view that possibly the actinium series may be a distinct primary one arising from a hypothetical isotope of uranium of  $a=240$ . This view was criticized† as being consistent only if this isotope has the same period as uranium I—an unlikely supposition. Adams‡ showed, however, that this proviso was unnecessary by explaining how the ratio of the ultimate parent of actinium to uranium I might be the same everywhere on the earth at any time although it would change progressively at a rate dependent on the difference in period of the two isotopes. Adams showed also that the end-product of the actinium series should by analogy with those of the other series have an atomic weight of 207. He assumes that a body  $z=91$ ,  $a=235$  produces actinuranium ( $z=92$ ,  $a=235$ ), which disintegrates to proto-actinium through uranium Y. On this view the atomic weight of actinium is 227. Recently Piccard§ has put forward a more detailed view with regard to the independent origin of actinium which resembles in part that of Adams. This scheme is given in Table I.

TABLE I.

Element.	Radiation.	$z$ .
Actinuranium I .....	$\alpha$	92
Uranium V.....	$\beta$	90
Uranium Z .....	$\beta$	91
Actinuranium II.....	$\alpha$	92
Uranium Y.....	$\beta$	90
Proto-actinium .....	$\alpha$	91
Actinium .....	$\beta$	89
Radio-actinium .....	$\alpha$	90

In favour of a scheme of this type are, in addition to the considerations aforesaid, (a) the fact that an element of even atomic number is expected from Aston's work to consist of several isotopes, and these in the case of uranium would

\* A. Piccard, *Arch. Sci. Phys. nat.* vol. xliv. p. 161 (1917).

+ F. Soddy & J. A. Cranston, *Proc. Roy. Soc.* vol. xciv. A, p. 384 (1918).

† E. Q. Adams, *J. Amer. Chem. Soc.* vol. xlii. p. 2205 (1920).

§ A. Piccard, *Phys. Zeit.* vol. xxiii. p. 1 (1922).

be expected to be radio-active, and (b) the fact that the atomic weight of ordinary uranium is in excess of an integer by about 0.18. Only about 0.10 of this can be accounted for by the energy expelled in the transformation of uranium I to radium  $\Omega'$  (the  $a$  of which is assumed to be 206.00). The remaining 0.08 could be explained by the existence of 4 per cent. of an isotope of  $a=240$  or 8 per cent. of one of  $a=239$ . In favour of the accepted view is (a) its simplicity, and (b) the fact that a dual change, involving the expulsion of  $\alpha$ -particles only, is rendered less unlikely than hitherto has been thought by the existence of a dual change involving the expulsion of  $\beta$ -particles only\*. Widdowson† and the writer have attempted to distinguish between these views by careful measurements of the relative activities of the products in an old uranium mineral, and have shown how difficult it is to come to a decision from such measurements.

Evidence from two pieces of experimental work, not yet, however, carried out, would distinguish between these opposing theories. The first of these is the determination of the atomic weight of proto-actinium. If this value were found to be a number not expressible by  $4n+2$ , where  $n$  is an integer, the ultimate parent of actinium could not be genetically connected with uranium I or uranium II if  $\alpha$  and  $\beta$  be the only particles expelled in a radio-active change. But if it were expressible by  $4n+2$ , it would be strong evidence in favour of the branch theory, and the value obtained would decide at which body the branching occurred‡. The second piece of work is a determination of the isotopes of uranium by Aston's methods. In absence of the evidence mentioned above, proof that uranium was a simple element would be evidence in favour of the view that the actinium series arises as a branch; proof that an isotope of atomic weight say 235 or 239, and in amount of the order of 5 per cent., would be evidence in favour of this isotope being the ultimate parent of the actinium series.

Besides the relation connecting atomic weight and the type of  $\beta$ -change, I have found empirical ones connecting (a) atomic weight and the periods of bodies in a  $\Sigma\alpha$  change, and (b) the periods of the four bodies comprising a  $\beta_1$

\* O. Hahn, *Zeit. Phys. Chem.* vol. ciii. p. 461 (1923); A. S. Russell, 'Nature,' vol. cxi. p. 704 (1923).

† W. P. Widdowson & A. S. Russell, to be published in *Phil. Mag.*; A. S. Russell, *loc. cit.*

‡ A view of the origin of actinium, put forward by S. Meyer (*Zeit. Phys. Chem.* vol. xcv. p. 428 (1920)), reconciles branching at uranium II with an  $a=227$  for actinium.



change. The first of these will now be described because it leads to an estimate of the atomic weight of actinium.

Several workers, notably Fajans \*, Swinne †, Carruthers ‡, and van den Broek §, have pointed out relations, on the lines of the Geiger-Nuttall relation, connecting atomic weights and the disintegration constants of periods of members of a group of isotopes. It appears to me, however, that simple relations of a quantitative kind can only be obtained if one makes a distinction between the kinds of successive change enumerated in § 2 above. Some of the exceptions to the Geiger-Nuttall relation and to Fajans's  $\alpha$ -ray and  $\beta$ -ray rules occur, I think, because this distinction has been lost sight of. My rule is much simpler and much less accurate than most of these, but unless it be fortuitous, which does not appear likely, it is sufficient for the purpose. It is that :

- (1) in a  $\Sigma\alpha$  change the period of a body is on the average about 800 times that of its successor,
- (2) the periods of isotopic members of  $\Sigma\alpha$  changes decrease in geometrical progression as the atomic weights decrease in arithmetical progression.

This rule may be illustrated by plotting the logarithms of the periods of the bodies composing the three known  $\Sigma\alpha$  changes against their atomic numbers. Three straight lines, approximately parallel, but not equally spaced, one for each series, are obtained. The average slope gives the result (1) above; the distance between the lines the result (2). On the average the periods of uranium, thorium, and actinium members are in the ratio of  $(80)^2 : 1 : \frac{1}{63}$ . Now if  $(80)^2 : 1$  correspond to a difference of atomic weight of 2,  $80 : 1$  corresponds to 1, and  $63 : 1$  consequently to 0.8. The atomic-weight of radio-actinium is therefore 227.2 or, by Rule VI. (a), 227, and this is also the atomic weight of actinium.

If these considerations be of weight and if  $\alpha$  and  $\beta$  be the only particles expelled in radio-active changes, there appears to be no escape from the view that the actinium series originates from an isotope of uranium with an atomic weight either of 235 or 239.

\* K. Fajans, *Phys. Zeit.* vol. xiv. p. 950 (1913).

† R. Swinne, *Phys. Zeit.* vol. xiv. p. 145 (1913).

‡ F. G. Carruthers, 'Nature,' vol. xcvi. p. 565 (1916).

§ A. van den Broek, 'Nature,' vol. xciii. p. 480 (1914); and 'Nature,' vol. xcvi. p. 677 (1916).

§ 5. *A Relation between the Periods of Bodies composing a  $\beta_1$  Change.*

The simple relation connecting bodies in  $\Sigma\alpha$  changes may be extended so that the periods of bodies in  $\beta_1$  changes may be roughly calculated by the following relation :

$k$ , defined by the relation

$$k \cdot \frac{P_{1st \alpha\text{-body}}}{P_{2nd \alpha\text{-body}}} = P_{1st \beta\text{-body}} \times P_{2nd \beta\text{-body}},$$

where  $P$  represents the period in minutes,

- (1) is of the same order (is possibly constant) for any given atomic number, and
- (2) diminishes by about  $\frac{1}{80}$  for each drop of 2 in atomic number.

The data on which this deduction is based are meagre, nevertheless they do not appear wholly fortuitous.

The values of  $k$ , calculated from experimental data, for the  $\beta_1$  changes  $UI \rightarrow Io$ ,  $Th \rightarrow ThX$ ,  $RaA \rightarrow RaC$ , and  $ThA \rightarrow ThC$  are given in Table II.

The changes  $AcA \rightarrow AcC$  and  $RaC' \rightarrow Ra\Omega'$  are not strictly comparable and so have not been included.

TABLE II.

$\beta_1$ Change.	Mean Value of $z$ .	$k$ (min <sup>-2</sup> ).
$UI \rightarrow Io$	91	17.7
$Th \rightarrow ThX$	89	0.21
$RaA \rightarrow RaC$	83	$8.7 \times 10^{-7}$
$ThA \rightarrow ThC$	83	$5.4 \times 10^{-7}$

The values of the two last depend upon the periods of  $RaC'$  and  $ThC'$  which are known only from the Geiger-Nuttall relationship\*. The real values of  $k$  may therefore be a hundred times smaller or larger. It is remarkable, however, that they are of the same order. The value of  $k$  for these changes calculated from the relation (2) immediately above is  $4.3 \times 10^{-7}$ .

§ 6. *The Upper Part of the Actinium Series.*

The scheme which in my view best represents the beginning of the actinium series is given in Table III.

I have followed Piccard† in naming the  $z=92$  isotopes

\* I have taken them to be  $3 \times 10^{-8}$  sec. and  $2 \times 10^{-12}$  sec. respectively.

† A Piccard, *loc. cit.*

TABLE III.

Position.	Element.	Period.	z.	Radiation.	a.
(1)	Actinuranium I	ca. $8 \times 10^6$ years	92	$\alpha$	239
(2)	Uranium Y <sub>1</sub>	28 hours	90	$\beta$	235
(3)	Uranium Y <sub>2</sub>	ca. 1 minute	91	$\beta$	235
(4)	Actinuranium II	$> 2 \times 10^6$ years	92	$\alpha$	235
(5)	Parent of Proto-actinium	$> 20$ years	90	$\beta$	231
(6)	Proto-actinium	$< 1.2 \times 10^4$ years	91	$\alpha$	231
(7)	Actinium	20 years	89	$\beta$	227
(8)	Radio-actinium	19.5 days	90	$\alpha$	227

actinuranium. I differ from both Piccard and Adams \* in not placing uranium Y in the position 5, and from Piccard in rejecting uranium V and uranium Z from the scheme. If uranium Y were in the position (5) it contravenes both Fajans's  $\beta$ -ray rule and Rule V. above. Deductions from analogies place it in position (2); experimental evidence does not decide between the two. Piccard's scheme (given in Table I.), in so far as it embraces uranium V and uranium Z, appears untenable, because (1) the existence of uranium V is doubtful †, (2) if it exists, its activity is initially only 2 per cent. of that of uranium X<sub>1</sub> and its period is too great to be the parent of uranium Z ‡, and (3) uranium Z is present only to the extent of 0.35 per cent. of the equilibrium amount of uranium X<sub>1</sub> §. The scheme above, however, postulates a new body, uranium Y<sub>2</sub>, with a period of less than a minute (because of Fajans's  $\beta$ -ray rule) corresponding to uranium X<sub>2</sub>. The period of actinuranium II is likely to be greater than that of uranium II because of Fajans's  $\alpha$ -ray rule. From the relation of § 5 it may be calculated if the period of uranium Y<sub>2</sub> be assumed 1 minute and that of actinuranium I be known. The period of the parent of proto-actinium should be greater than 20 years, because of Rule V.; that of proto-actinium must be as given since the period  $1.2 \times 10^4$  years is based on the growth of that element from purified uranium I + uranium II on the assumption that only the short-lived uranium Y lies between. The periods of actinuranium I and actinuranium II are estimated from the considerations of the next paragraph.

\* E. Q. Adams, *loc. cit.*

† O. Hahn, *Phys. Zeit.* vol. xxiii. p. 146 (1922); F. Soddy & A. S. Russell, *Phil. Mag.* vol. xviii. p. 858 (1909).

‡ A. Piccard & E. Stahel, *Phys. Zeit.* vol. xxiv. p. 80 (1923).

§ O. Hahn, *Zeit. Phys. Chem.* vol. ciii. p. 461 (1923); A. S. Russell, 'Nature,' vol. cxi. p. 704 (1923).

§7. *The Periods of Actinuranium I and Actinuranium II.*

A determination of the ranges of the  $\alpha$ -particles of these bodies would enable an estimate of their periods to be obtained from the Geiger-Nuttall relation. This difficult experiment appears to be the only feasible one at present towards that end. It is to be expected, however, that bodies  $z=92$ ,  $a=240$ ;  $z=92$ ,  $a=239$ , and  $z=92$ ,  $a=238$ , would have periods in decreasing order of magnitude. The relation which exists between isotopic members of  $\Sigma a$  change is inapplicable to these independent isotopes. For want of a better I offer this suggestion. It was shown in fig. 3 above that if the series 220 (the thorium series) had originated from an isotope of uranium, its atomic weight would have been 240. Suppose then that this body  $z=92$ ,  $a=240$ , if it existed had the period of thorium, namely  $1.31 \times 10^{10}$  years. The body  $z=92$ ,  $a=239$ , would then probably have a period the geometric mean of this and that of uranium I, *i.e.*, about  $7.8 \times 10^9$  years. It is perhaps a bold supposition, but the fact that thorium's  $\beta$ -ray product, mesothorium, has a greater period than that expected from the  $\beta$ -ray product of  $z=92$ ,  $a=240$ , is not an argument against it.

If actinuranium I has a period of  $7.8 \times 10^9$  years, and if the value of the ratio of the activities of proto-actinium to ionium in equilibrium be accepted as 3 per cent. \*, then this body must be present to the extent of  $3 \times \frac{7.8 \times 10^9}{4.7 \times 10^9}$ , *i.e.*, about 5 per cent. in ordinary uranium.

It may be possible to estimate this percentage accurately in another way by comparing the ratio of uranium to radium in an old mineral obtained directly by analysis with that calculated from the experimental values of the periods of uranium and radium. But at present these are not known sufficiently accurately to give a decision.

The period of actinuranium II may be estimated in three ways :

- (1) As  $8.2 \times 10^7$  years from the relation of § 5† assuming  $P_{U_{X_2}}$  to be 1 minute,  $P_{U_X}$ , 28 hours, and  $P_{AcU_{II}}$   $7.8 \times 10^9$  years.
- (2) As  $1.4 \times 10^7$  years from the relation

$$\frac{P_{AcU_{II}}}{P_{U_{II}}} = \sqrt[4]{\frac{P_{U_I}}{P_{U_{II}}}}$$

- (3) As  $> 2 \times 10^6$  by Fajans's  $\alpha$ -ray rule.

\* O. Hahn, *Berichte*, vol. lii. B. p. 1812 (1919); W. G. Guy & A. S. Russell, to be published in Journ. Chem. Soc.

§8. *Radio-active Isotopes and Isotopes of Inactive Elements.*

It is of interest to compare some properties of a group of radio-active isotopes with those of a group of isotopes belonging to a common element.

(1) Aston has shown that an inactive element of even atomic number may have isotopes both even and odd in atomic weight. This holds also for radio-active isotopes if actinium have the atomic weight assigned to it in this paper.

(2) The same author has shown that a common element of odd atomic number consists of either one or two isotopes of odd atomic weight. If there be two isotopes they differ in atomic weight by 2. This does not hold at all for radio-active isotopes, *cf.* the isotopes of proto-actinium, bismuth, etc.

(3) Aston's results show that isotopes of even atomic number may differ by 8 and possibly 10 or 12 units of atomic weight. Radio-active isotopes do not appear to differ by more than 8. It is possible that the reason why this number is not exceeded is connected with the stability of the nucleus. None of the isotopes of common element whose existence appears at the moment to contravene this is regarded as firmly established by Aston himself.

I have made use of the difference described under (2) above to put forward a suggestion that is, I think, new. It is obvious that radio-active isotopes may be brought into line with inactive isotopes with respect to this matter if the following be true:—*The end-products of all radio-active series are inactive isotopes.* This idea is tenable, I think, without the implication that such inactive isotopes have been necessarily produced as a result of radio-active disintegration.

Simple analysis has shown that elements of atomic number 80, 79, and lower numbers do not appear to have isotopes in the radio-active series. Possible end-products are thus confined to isotopes of atomic numbers 83, 82, and 81. Some of these have been shown marked with a black circle in fig. 2 above. In series 221 the lower portion of the  $\beta_1 \beta_2$  path is incomplete. At the  $z=83, a=209$ , body a branch may occur, but since the product  $z=84, a=209$ , is not possible because of Rule IV., this branch of the series may end at  $z=83, a=209$ ; the main product of the branching  $z=81, a=205$ , cannot be transformed (as symmetry indicates) into  $z=82, a=205$ , because of Rule IV., and consequently the main portion of the series ends at  $z=81, a=205$ . It is possible also for part of series 219 to end at  $z=81, a=203$ , without contravening any of the guiding rules of this paper.

Possible end-products are tabulated in Table IV. In the third column are given the atomic weights of possible end-products, and in the fourth those *to be expected* experimentally from Aston's investigations.

TABLE IV.

Element.	<i>z</i> .	Values of <i>a</i> deduced from the series				Values of <i>a</i> to be expected experimentally.
		222	221	220	219	
Thallium ...	81	—	205	—	203	203, 205
Lead .....	82	206, 210	209 ?	208, 208	207	206, 208, 210, etc.
Bismuth ...	83	—	209	—	—	209

It is assumed here that thallium's inactive isotopes are 203 and 205, because this element has an odd atomic number and its experimental atomic weight is 204. Bismuth has probably only one inactive isotope, 209; if it has a second it is more likely to be 207 than 211. The postulates of Table IV. are not inconsistent with the research of Soddy and Hyman \*, who found a trace of thallium but no bismuth in a specimen of thorite containing only 0.85 per cent.  $U_3O_8$ , or with that of Merton †, who found a trace of thallium with a spectrum slightly different from that of ordinary thallium in pitchblende residues. The known limits of atomic weights of radio-active isotopes are given for reference in Table V.

TABLE V.

Element.	<i>z</i> .	Limits of <i>a</i> .	<i>a</i> of longest-lived or common isotopes.
Uranium .....	92	239-231	234, 238, 239 ?, 235 ?
Proto-actinium .....	91	235-231	231
Thorium .....	90	235-227	232, 233 ?
Actinium.....	89	227-223	227
Radium .....	88	226-223	226
Radon .....	86	222-219	222
Polonium ...	84	218-210	210
Bismuth .....	83	214-207 ?	209, 207 ?
Lead .....	82	214-206	206, 208, 210, 209 ?, 207 ?
Thallium.....	81	210-203	203, 205
Mercury .....	80	204-197	197-200, 202, 204

\* F. Soddy & H. Hyman, Journ. Chem. Soc. vol. cv. p. 1402 (1914).

† T. Merton, Proc. Roy. Soc. vol. xevi. A. p. 394 (1929).

The rarest of all known longest-lived or common isotopes except radon is polonium. Analysis shows that no isotope of longer period is likely. The shortness of the period suggests that polonium can never be obtained in sufficient concentration to be treated as a common element. Its existence, detectable only by the methods of radio-activity, helps to justify the assumption often made that missing elements have not been discovered, less because the search for them has been poor than for the fact that, if formed at all in nature, they are too unstable to be detected by the balance.

Experimental work on uranium  $Y_2$ , on the hypothetical series 221, and on the nature of branching in all series, is in progress.

### *Summary.*

(1) In discussing analogies or general relations between the three disintegration series it has been found most advantageous to regard a series as made up of three types of successive changes, and to keep these distinguished.

(2) It is deduced that there are probably only four independent disintegration series. The path of disintegration of each of these is given.

(3) Simple empirical relations between the periods of bodies comprising a  $\Sigma\alpha$  change and between those comprising a  $\beta_1$  change are given.

(4) It is concluded that actinium arises from an isotope of uranium with an atomic weight of 239, present to the extent of about 5 per cent. Estimates of the periods of the bodies which precede proto-actinium in its series are given.

(5) Radio-active isotopes are compared with those of inactive elements and a suggestion with regard to the existence of end-products other than those of isotopes of lead is put forward.

Dr. Lee's Laboratory,  
Christ Church, Oxford.  
June 1923.

LXXIII. *Motion of Electrons in Helium.* By J. S. TOWNSEND, M.A., F.R.S., Wykeham Professor of Physics, Oxford, and V. A. BAILEY, M.A., D.Phil., The Queen's College, Oxford\*.

1. **I**N previous communications to the Philosophical Magazine† we have described a method of determining the motion of electrons in various gases, and we have recently used the method to determine the motion in helium.

The experimental part of the investigation consists in determining the velocity  $W$  of a stream of electrons in the direction of a uniform electric force  $Z$ , and the velocity of agitation  $u$ . For this purpose we found it convenient to use two instruments, one being suitable for the measurement of the velocities in gases where the stream of electrons has a moderate lateral diffusion, and the other suitable for gases like argon where the lateral diffusion of the stream is very large. A full description of these two instruments is given in the account of our researches on Argon and Hydrogen‡. The former instrument was arranged so that a stream of electrons, after passing through a narrow slit, was received on three electrodes at a distance of 4 centimetres from the slit, and in the latter the receiving electrodes were 2 centimetres from the slit.

With helium, for the smaller values of the ratio  $(Z/p)$  of the electric force  $Z$  to the pressure of the gas  $p$ , the determinations were made with the instrument in which the electrodes were 4 centimetres from the slit, and for the larger values of the ratio  $Z/p$  the determinations were made with the other instrument. For certain ranges of forces and pressures it was possible to make determinations with both instruments, and concordant results were obtained.

2. In these experiments two specimens of helium were used—one which was obtained from a natural source, and the other obtained by heating thorianite. The velocities of the electrons were found to be almost exactly the same in the two specimens.

In each case the gas was purified by means of charcoal cooled by liquid air. The apparatus was tested by exhausting it to 1/100 of a millimetre pressure, and no leak was detected by a McLeod gauge when the pressure

\* Communicated by the Authors.

† Phil. Mag. December 1921, March, June, and November 1922.

‡ Phil. Mag. November 1922.



was observed at intervals during several weeks. The connexion to the pump and mercury gauges was made through tubing cooled by liquid air, in order to reduce any effect which might be due to mercury vapour. It was not found, however, that this precaution to remove mercury vapour made any appreciable difference to the results of the experiments, which may have been due to the fact that all the electrodes and metal rings in the apparatus were silver-plated and absorbed mercury vapour.

3. The agreement between the values of  $W$  and  $k$ , obtained with different forces and pressures when the ratio  $Z/p$  was constant, shows that there could have been no notable effect due to an impurity unless the amount of the impurity were proportional to the pressure of the gas. It therefore follows from the results of the experiments that the mercury vapour had no appreciable effect, as it would be impossible for the vapour pressure in the apparatus to be proportional to the gas pressure. This result was tested with considerable care after most of the observations were made in the ordinary manner. The method of removing mercury vapour recommended by Professor Merton was used, which consists in absorbing the vapour by silvered glass tubing, the silver being deposited by a discharge from silver electrodes. Before making these experiments the whole apparatus was taken down and all the electrodes and metal rings in the measuring instruments were replated with silver so as to expose the gas to a large surface of pure silver. The instrument was then connected to the pump and gauges through the silvered glass tubing and a tap which was turned off immediately after the pressure in the apparatus had been measured. The apparatus was exhausted and washed out with helium to remove traces of impurities. The helium used in these experiments was pumped into a tube filled with charcoal which was cooled with liquid air, and the gas was kept in the charcoal tube for an hour before it was admitted to the apparatus. Measurements of  $W$  and  $k$  were made with the gas at the pressures 20, 10, and 5 millimetres, and they were found to be almost exactly the same as those made in the ordinary manner when no special precautions were taken to remove mercury vapour.

4. The results of the experiments are given in Table I., where  $p$  is the pressure of the gas in millimetres,  $Z$  the electric force in volts per centimetre,  $W$  the velocity of the electrons in the direction of the electric force in centimetres per second, and  $k$  the factor by which the energy of

agitation of the electrons exceeds the energy of agitation of an equal number of molecules of a gas at 15° C.

TABLE I.

$p.$	$Z.$	$Z/p.$	$k.$	$W \times 10^{-5}.$
240	3.15	.0131	1.75	1.07
160	2.1	.0131	1.79	1.14
240	6.3	.0262	...	1.50
160	4.22	.0263	2.52	1.56
120	4.2	.035	3.01	1.73
160	8.43	.0527	3.93	2.15
120	6.3	.0525	3.90	2.12
80	4.22	.0527	3.76	2.30
120	12.6	.105	6.65	2.92
80	8.43	.105	6.46	3.06
80	16.9	.21	12.0	4.08
40	8.4	.21	11.6	4.00
20	4.22	.21	11.8	3.95
20	8.45	.42	22.8	5.3
10	4.2	.42	23.3	5.0
20	16.9	.845	44.0	7.6
10	8.4	.84	45.3	7.4
10	16.9	1.69	91	11.4
7.5	12.6	1.68	93	11.5
7.5	21.0	2.8	134	16.4
5	16.9	3.38	145	19.6
5	21.0	4.2	158	25.2
5	26.5	5.3	177	32.0

The numbers given in the table are the means of several experiments which were in good agreement. Those corresponding to the lower values of the ratio  $Z/p$  from .0131 to .105 were obtained with the instrument in which the receiving electrodes were 4 centimetres from the slit, and most of the other numbers were obtained with the other instrument.

The curves given in figs. 1 and 2 represent the values of  $W$  and  $k$  for helium in terms of the ratio  $Z/p$ .

Fig. 1.

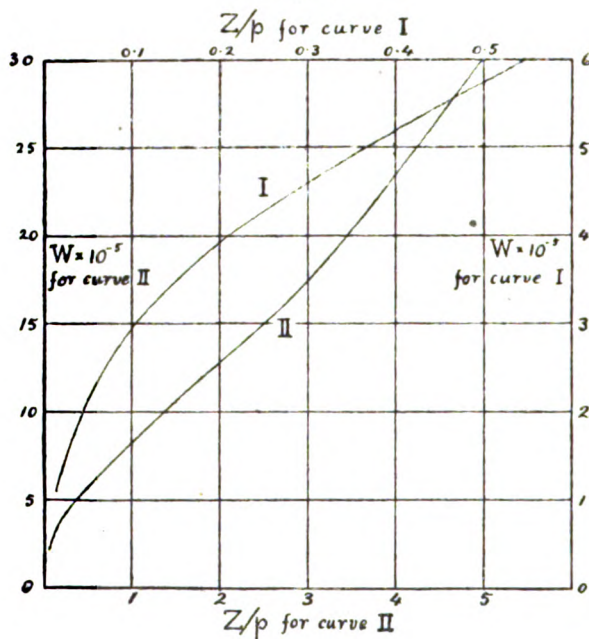
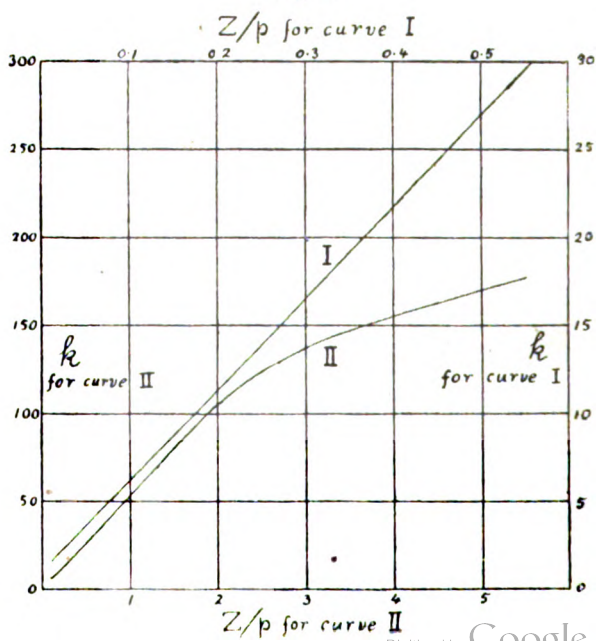


Fig. 2.



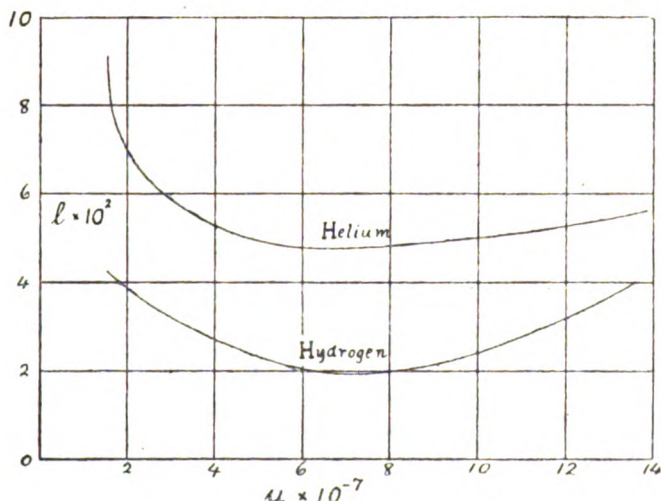
5. The velocity of agitation  $u$ , the mean free path  $l$ , and the proportion  $\lambda$  of the energy of an electron which is lost in a collision, found from the above values of  $k$  and  $W$  by the formulæ  $u = 1.15 \times 10^7 \sqrt{k}$ ,  $W = .815 Z e l / m u$ , and  $\lambda = 2.46 W^2 / u^2$ , are given in Table II. The values of  $l$  are for the gas at 1 millimetre pressure.

TABLE II.

$Z/p.$	$k.$	$W \times 10^{-5}.$	$u \times 10^{-7}.$	$l \times 10^2.$	$\lambda \times 10^4.$
.013	1.77	1.11	1.53	9.14	1.30
.02	2.12	1.33	1.68	7.8	1.56
.05	3.68	2.14	2.21	6.6	2.3
.1	6.2	2.96	2.87	5.95	2.6
.2	11.3	3.93	3.87	5.3	2.55
.5	27	5.74	5.96	4.8	2.3
1.0	53	8.25	8.4	4.85	2.4
1.5	79.5	10.5	10.3	5.0	2.6
2.0	105	12.7	11.8	5.25	2.85
2.5	124	15.0	12.8	5.4	3.4
3.0	137	17.5	13.5	5.5	4.15
4.0	152	23.5	14.2	5.85	6.75
5.0	172	30.2	15.1	6.4	9.8

6. In order to compare the mean free paths of electrons in helium with the mean free paths in hydrogen, the values of  $l$  for the two gases at a millimetre pressure corresponding

Fig. 3.



to velocities of agitation  $u$  from  $1.5 \times 10^7$  to  $14 \times 10^7$  cms. per sec. are given by the curves in fig. 3. The free path of

an electron in helium is about twice as long as the free path in hydrogen, but if the free paths were deduced from the viscosities of the gases the lengths would be in the proportion of about 3 to 2. It will be noticed that there is an increase in the mean free path in helium from  $5 \times 10^{-2}$  to  $9 \times 10^{-2}$  cm. when the velocity of the electron decreases from  $5 \times 10^7$  to  $1.5 \times 10^7$  cms. per sec. Judging from the direction of the curve, it is probable that there would be a further increase in  $l$  if the velocity were reduced below the value  $1.5 \times 10^7$ . This velocity corresponds to a potential difference of .065 volt.

In helium the mean free path is nearly constant for velocities between  $10^8$  and  $5 \times 10^7$  cms. per sec., but in argon the mean free path increases from about  $18 \times 10^{-2}$  cm. when the velocity is  $10^8$  to about  $110 \times 10^{-2}$  cm. when the velocity is  $5 \times 10^7$ . Thus the increase in the free path as the velocity diminishes occurs for smaller velocities in helium than in argon.

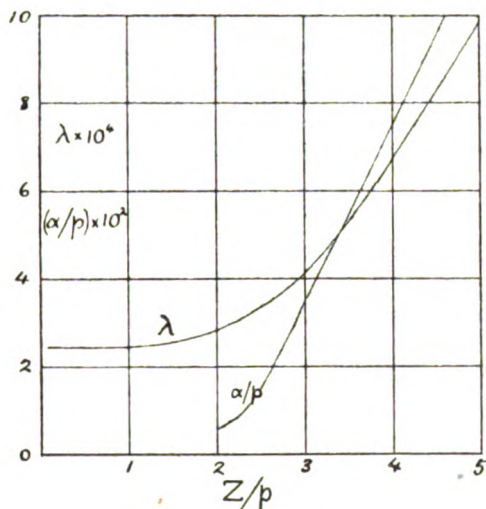
Experiments are at present being made with neon, but a sufficient number of results have not yet been obtained to compare this gas with helium and argon.

7. The numbers in the last column of Table II. show that the proportion of the energy of an electron lost in a collision is nearly constant for the range of velocities from  $2 \times 10^7$  to  $10^8$  cms. per sec. This proportion is about  $2.5 \times 10^{-4}$ , and is approximately the same as the average proportion of energy which would be lost when a small particle of mass  $m$  collides with a perfectly elastic sphere of mass  $M$  if  $m/M$  were equal to the ratio of the mass of an electron to the mass of a helium atom. This, however, does not justify the hypothesis that the helium atom resembles an elastic sphere, since the variations in  $l$  are not consistent with such an hypothesis.

For velocities greater than  $10^8$  and values of  $Z/p$  greater than 2, the values of  $\lambda$  increase considerably. It may be seen that this increase is due to ionization by collision by comparing the curves representing  $\lambda$  and  $\alpha/p$  in terms of  $Z/p$ . These curves are given in fig. 4. The quantity  $\alpha$  has the usual signification, namely, the average number of molecules ionized by an electron in moving through a centimetre in the direction of the electric force. The values of  $\alpha/p$  which are given are those obtained in an investigation made with Mr. Ayres of the effects of ionization by collision, which will be published shortly. The same specimens of helium were used in all these determinations,

and the same precautions were used to eliminate mercury vapour.

Fig. 4.



*Note on the Determination of W.*

In the accounts of our previous experiments we have mentioned that the velocities  $W$  determined with different forces and pressures, when the ratio  $Z/p$  is constant, are practically the same, provided the streams of electrons are of moderate divergence. But with very widely diverging streams the values obtained for  $W$  are smaller, when calculated by the same method. We regarded this as being probably due to part of the stream being deflected by the transverse magnetic force beyond the boundary of the receiving electrodes. Further experiments have shown that the discrepancy would not be eliminated by increasing the area of the receiving electrodes, and that it arises from a secondary effect on the stream due to the electrodes, which becomes appreciable when the coefficient of diffusion  $K$  of the electrons is very large compared with the velocity  $W$  in the direction of the electric force. The discrepancy is seen by considering the results of the set of experiments with hydrogen given in Table III., which were made with an instrument where the receiving electrodes were 4 centimetres from the slit. In this table  $R$  is the ratio of the charge received by the central electrode  $E_2$



to the total charge received by the three electrodes  $E_1$ ,  $E_2$ , and  $E_3$  when no magnetic force is acting.

TABLE III.

$p$ .	$Z$ .	$Z/p$ .	$R$ .	$W \times 10^{-5}$ .	$k$ .
10	34	3.4	.53	21.5	20.4
5	17	3.4	.394	21.8	20.2
2.53	8.5	3.36	.29	21.5	20.2
1.24	4.25	3.42	.214	19.0	20.1

The ratio  $R$  is a function of  $W/K$  or  $41Z/k$ , and the relation connecting  $R$  and  $Z/k$  is given by means of a curve as shown in fig. 3 on p. 1039 of the *Philosophical Magazine* of November 1922. The experiments show that when the ratio  $Z/p$  is constant, the values of  $W$  obtained with different forces and pressures are in good agreement when  $R$  is greater than .29, but with a very widely diverging stream ( $R=.21$ ) the value of  $W$  is about 12 per cent. less than that obtained when  $R$  is greater than .29.

In this method of measuring the velocity  $W$  from observations of the magnetic deflexion of the centre of the stream, the determinations should be independent of the divergence of the stream when the divergence is not very large, and several sets of experiments have shown that when  $Z/p$  is constant the velocities obtained with different forces and pressure are practically the same when  $R$  is greater than .24 or  $Z/k$  greater than .28. These values are therefore the right ones, and the correction which must be applied when the stream is very divergent is easily found experimentally. This conclusion is in agreement with the fact that the four determinations of  $k$  given in Table III. are the same, since this indicates that the velocity in the last experiment should be the same as in the others.

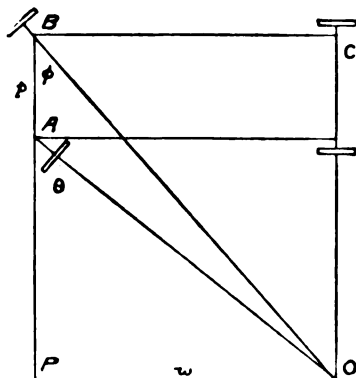
With the second instrument, where the receiving electrodes are 2 centimetres from the slit, it will be seen from the curves giving  $R$  in terms of  $Z/k$  that  $R$  is .33 when  $Z/k$  is .28. Thus, although this instrument is convenient for measuring  $k$  when the streams of electrons are very widely divergent, it is necessary to correct the values of  $W$  when  $R$  is less than .33. In the experiments with monatomic gases the ratios  $R$  were in many cases less than this, and the corresponding values of  $W$  which we have given for argon and helium are the corrected values.

LXXIV. *The Automobile Steering Linkage.* By P. CORMACK,  
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Dublin\*.

1. *The Concurrent Equation.*

IN order that the wheels of a motor-car may roll without side-slip of the tyres on the ground, the plans of the axes of the road wheels must be concurrent. In fig. 1 the axes AO, BO, of the steering wheels, and the common axis CO of the rear wheels, intersect at O: the car turns about O as centre, this being the unique turning-point which allows each wheel to pursue its natural rolling path. There is now a simple relation between  $\theta$  and  $\phi$ , the angles of deflexion of

Fig. 1.



the inner and the outer steering wheels. Let  $p$  denote the pitch of the steering pivots AB, and let  $w$  denote the wheel-base PO. From fig. 1,

$$AB = PB - PA = PO \cot \phi - PO \cot \theta,$$

whence  $\cot \phi - \cot \theta = p/w$ . . . . . (1)

It follows readily by the method of indirect proof that when the deflexions of the steering wheels satisfy (1) the wheel axes are concurrent.

For very small values of  $\theta$  and  $\phi$ , equation (1) becomes

$$1/\phi - 1/\theta = p/w,$$

or, in other words, we have,

$$\text{Lit. } [(\theta - \phi)/\theta\phi] = p/w. \quad \text{. . . . . (2)}$$

$\theta=0$

\* Communicated by the Author.



2. *Property of Quadrilateral.*

The usual automobile steering linkage is shown in figs. 2 and 3. In its mean position, fig. 2, A and B are the fixed steering pivots about which the stub-axles of the steering wheels with their attached steering arms AD, BC, turn. CD is the coupler or tie-rod joining the ends of the steering arms.

Let us drop AM, BN, perpendicular to CD, cutting CD produced in M and N, and consider now the triangles ADM, BCN as plates attached to and partaking of the movements of the steering arms. We shall use  $t$  to denote AM the depth of the steering quadrilateral, and  $s$  to denote the length MD.

Fig. 3 shows the steering linkage with the arm AD (and in consequence AM and the outer steering wheel) deflected

Fig. 2.

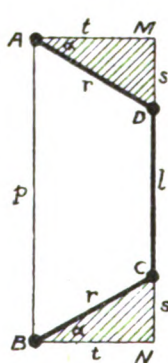
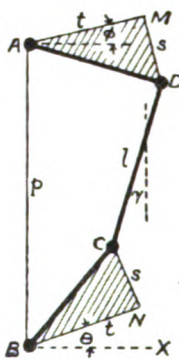


Fig. 3.



through an angle  $\phi$ , and with the arm BC (and in consequence BN and the inner steering wheel) deflected through an angle  $\theta$ . Denoting by  $\gamma$  the angle which CD makes with AB, we have by projection on AB

$$t \sin \theta + s \cos \theta + l \cos \gamma + s \cos \phi - t \sin \phi - p = 0,$$

while by projection on BX we have

$$t \cos \theta - s \sin \theta + l \sin \gamma - s \sin \phi - t \cos \phi = 0.$$

Writing out the value of  $\cos^2 \gamma$  from the first equation and the value of  $\sin^2 \gamma$  from the second equation and adding the two results, we eliminate  $\gamma$  and obtain the following equation :

$$s^2[1 - \cos(\theta - \phi)] - s[p(2 - \cos \theta - \cos \phi) + 2t \sin(\theta - \phi)] + pt(\sin \theta - \sin \phi) - t^2[1 - \cos(\theta - \phi)] = 0. \quad (3)$$

If both  $s$  and  $t$  be taken negative, this equation is also true for the external quadrilateral in which the length of the coupler is greater than the pitch of the steering pivots and in which the coupler is placed in front of the cross-member which carries the steering pivots.

It may be noted that the ratio  $s/t$  is  $\tan \alpha$ , where  $\alpha$  is the angle made by the plan of the steering arm with the path of the wheel.

It is evident that for given values of  $p$ ,  $w$ , and  $t$  (or  $s$ ) we can design the steering quadrilateral to give correct steering for any assigned value of  $\theta$ ; for by determining  $\phi$  from (1) and then substituting in (3) we can find  $s$  (or  $t$ ) and hence draw the gear.

### 3. Property of Quadrilateral, neglecting Effect of Coupler Obliquity.

Neglecting the effect of coupler obliquity is equivalent to taking  $s$  and  $t$  to be negligible in comparison with  $p$ . Dividing (3) throughout by  $p$  and neglecting the terms containing  $s/p$  and  $t/p$ , we obtain  $s/t$  or

$$\tan \alpha = (\sin \theta - \sin \phi) / (2 - \cos \theta - \cos \phi),$$

an equation which may be readily deduced directly.

When  $\theta$  and  $\phi$  satisfy (1) the limiting value for  $\theta=0$  of  $(\sin \theta - \sin \phi) / (2 - \cos \theta - \cos \phi)$  is  $p/w$ . For writing the fraction equal to

$$\frac{(\theta - \frac{1}{6}\theta^3 + \dots) - (\phi - \frac{1}{6}\phi^3 + \dots)}{2 - (1 - \frac{1}{2}\theta^2 + \dots) - (1 - \frac{1}{2}\phi^2 + \dots)}$$

we get its limiting value to be the same as that of

$$\text{or} \quad \frac{(\theta - \phi) / (\frac{1}{2}\theta^2 + \frac{1}{2}\phi^2)}{\frac{2(\theta - \phi)}{\theta\phi} \left/ \left[ \frac{\theta - \phi}{\theta\phi} \cdot (\theta - \phi) + 2 \right] \right.},$$

which, making use of (2), is  $p/w$ .

Hence for correct steering to obtain with small deflexions of the steering wheels we must make  $\alpha = \tan^{-1} p/w$  or, what is equivalent, we must make the steering arms converge to a point midway between the front and back axles.

### 4. Limiting Value of Steering-arm Angle, Obliquity of Coupler included.

The accurate gear equation is (3). Dividing (3) throughout by  $\sin \theta - \sin \phi$  and taking the limiting form of each

term as  $\theta$  approaches zero and when  $\theta$  and  $\phi$  satisfy (1), we get

$$0 \cdot s^2 - s(p \cdot w/p + 2t) + pt - 0 \cdot t^2 = 0,$$

from which

$$s/t = p/(w + 2t), \quad . \quad . \quad . \quad . \quad . \quad (4)$$

or again

$$s/t = (p - 2s)/w = l/w.$$

Hence for correct steering to obtain when running straight or in a curve of very large radius, we must make  $\alpha = \tan^{-1} l/w$  or  $\tan^{-1} \frac{1}{2} p/(\frac{1}{2} w + t)$ , that is, the steering arms must converge to a point at a distance  $t$  from the centre of the car—in front of the centre for an external quadrilateral for which  $t$  is negative, and to the rear of the centre for an internal quadrilateral for which  $t$  is positive.

### 5. An Approximate Equation for Design of Quadrilateral.

An empirical equation simpler than (3) and sufficiently accurate for practical purposes, suggested by the above form for (3) when  $\theta = 0$ , is

$$\tan \alpha = \frac{p}{2(w + 2t)} [1 + \cos 1 \cdot 63 \theta]. \quad . \quad . \quad . \quad (5)$$

It must be remembered that a negative value for  $t$  must be introduced in (5) for an external quadrilateral. Instead of the depth  $t$  of the quadrilateral, the length  $r$  of the steering arm may be used without appreciable error; so that we have for a working formula

$$\tan \alpha = \frac{p}{2(w + 2r)} [1 + \cos 1 \cdot 63 \theta]. \quad . \quad . \quad . \quad (6)$$

As an illustrative example we shall design a gear for a car having a wheel-base of 120 inches; pitch of steering pivots 48 inches; length of steering arm 7 inches; wheel axes to be concurrent at  $30^\circ$  deflexion of inner wheel.

We have, substituting in the design formula (6)

$$\tan \alpha = \frac{48}{268} (1 + \cos 48^\circ 54') = \cdot 2969,$$

or  $\alpha = 16\frac{1}{2}^\circ$ . (If an external quadrilateral were required we should have

$$\tan \alpha = \frac{48}{2(120 - 14)} (1 + \cos 48^\circ 54') = \cdot 3752,$$

which gives  $\alpha = 20\frac{1}{2}^\circ$ .)

For small deflexions, this gear will give the steering-wheel

axes intersecting at a distance  $w_0$  behind the front axle, given by

$$\tan \alpha = \frac{p}{2(w_0 + 2r)} (1 + \cos 0^\circ),$$

from which  $w_0 = 147$  inches.

Taking the maximum angle of lock for this car to be  $40^\circ$ , for this deflexion of the inner steering wheel the front stub axes intersect at a distance  $w_m$  behind the front axle given by

$$\tan \alpha = \frac{p}{2(w_m + 2r)} (1 + \cos 1.63 \times 40^\circ),$$

from which  $w_m = 100$  inches.

The gear thus gives the steering-wheel axes intersecting 27 inches behind the back axle at the beginning of the steering movement, intersecting on the back axle when the deflexion of the inner wheel is  $30^\circ$ , and intersecting 20 inches in front of the rear axle at the end of the steering movement. To design a gear to give the point of intersection of the steering-wheel axes as much behind the back axle at the beginning of the steering movement (deflexion  $0^\circ$ ) as it is in front of the rear axle at the end of the steering movement (deflexion  $\psi$ ), we have from (6)

$$w_0 + 2r = p(1 + \cos 0^\circ)/2 \tan \alpha,$$

$$w_m + 2r = p(1 + \cos 1.63\psi)/2 \tan \alpha,$$

and since we require  $w = \frac{1}{2}(w_0 + w_m)$  we get

$$w + 2r = p(3 + \cos 1.63\psi)/4 \tan \alpha$$

$$\text{or} \quad \tan \alpha = \frac{p}{4(w + 2r)} [3 + \cos 1.63\psi]. \quad \dots \quad (7)$$

With the above dimensions this gives a setting of  $17^\circ$  for the steering arm angle  $\alpha$ .

The design formula (5) may be used to calculate the performance of an existing gear. Take, for example, a car having  $p = 52$  ins.,  $w = 100$  ins.,  $t = 6$  ins.,  $s = 2$  ins. To find the angle  $\theta$  at which correct steering obtains, we have  $\tan \alpha = s/t = 2/6$ , so that substituting in (5)

$$1/3 = 52(1 + \cos 1.63\theta)/2(100 + 12),$$

whence  $\theta = 39^\circ$ .

Historically, the gear with steering arms converging to the centre of the back axle is of interest. For a general notion of the performance of this gear, for which  $\tan \alpha = p/2w$ ,

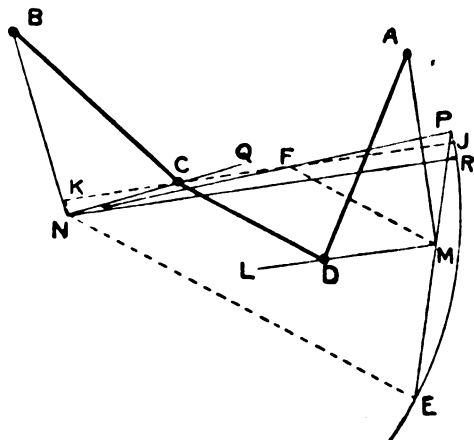
we may neglect  $t$  in (5). We then obtain  $1 = 1 + \cos 1.63\theta$ , from which  $\theta = 55^\circ$ , an angle much outside the working range usual in motor-car practice.

The inclinations sometimes given to steering pivots and to stub-axes do not appreciably affect the design of the linkage; the actual angle of deflexion of the stub-axis is sensibly the same as the angle in plan, while in plan the path of the steering-arm end is an ellipse which differs but little from the actual circular path.

#### 6. Graphical Solution of Design Problem.

It may not be without interest to give a graphical solution of (3) when the known magnitudes are  $\theta$ ,  $\phi$ , and  $t$ . The given data enable us to draw the lines AB, AM, BN, and the perpendiculars MDL, NCQ at M and N. figs. 3 and 4. The

Fig. 4.



problem evidently now is to fit in CD between ML and NQ so that  $NC = MD$  and  $NC + CD + DM = AB$ . From N draw NR parallel to ML and make NR equal to AB, the pitch of the steering pivots. Draw NP bisecting the angle QNR and from R drop RP perpendicular to NP. Join PM.

With centre N and radius NR describe a circle cutting PM in E. Join EN and through M draw MF parallel to EN cutting NP in F. Through F draw FC parallel to MD cutting NQ in C. Through C draw CD parallel to MF cutting ML in D. Join BC, AD. Then BCDA is the required linkage.

The construction evidently makes  $NC = CF = MD$ . Draw

NK parallel to RP and let CF be produced to meet RP in J and NK in K. The triangles PNE, PFM are similar, therefore

$$NE : FM :: NP : FP.$$

Again, since the triangles PNR, PFJ are similar,

$$NP : FP :: NR : FJ.$$

Hence  $NE : FM :: NR : FJ.$

And since  $NE = NR$  we therefore have  $FM = FJ$ . But  $FM = CD$ , hence  $CD = FJ$ .

Since  $NC = CF$  and the angle FNK is a right angle, the circle centre C which passes through F and N will pass through K so that  $KC = NC$ .

Hence finally we have

$$NC + CD + DM = KC + CF + FJ = KJ = NR = AB$$

as required.

LXXV. *On the Decay of Vortices in a Viscous Fluid.*

By G. I. TAYLOR, F.R.S.\*

A NUMBER of problems have been solved in which the rate of decay of small oscillations or waves in a viscous fluid has been found, but the simplification brought about by considering only small motions excludes many of the most important problems of fluid motion. On the other hand, when the complete equations of motion involving terms containing the square of the velocity have been used very few solutions have been obtained. Certain problems in steady motion †, problems concerning the two-dimensional motion of a viscous liquid when it is symmetrical about an axis ‡, and problems concerning laminar motion parallel to a plane § probably complete the list.

The object of the present paper is to draw attention to a class of cases in which solutions of the complete equations

\* Communicated by the Author.

† Flow through a pipe or between concentric cylinders.

‡ See Taylor, 'Reports and Memoranda of the Advisory Committee for Aeronautics, 1918-19.' Also Terazawa, 'Report of Aeronautical Research Institute,' Tokio, 1922.

§ See Lamb, 'Hydrodynamics,' chap. xi.

of motion, including the "inertia" terms, may be obtained for two-dimensional viscous flow.

If  $\psi$  represents the Stream Function so that the components of velocity are

$$u = -\frac{\partial\psi}{\partial y}, \quad v = \frac{\partial\psi}{\partial x},$$

the vorticity at any point is

$$\zeta = \nabla^2\psi.$$

The equation of motion may be written

$$\left(\frac{\partial}{\partial t} - \frac{\partial\psi}{\partial y} \frac{\partial}{\partial x} + \frac{\partial\psi}{\partial x} \frac{\partial}{\partial y} - \nu \nabla^2\right) \nabla^2\psi = 0, \quad (1)$$

where  $\nu$  is the coefficient of kinematic viscosity. Now consider functions which satisfy the equation

$$\nabla^2\psi = K\psi,$$

where  $K$  is a constant. These functions will also satisfy (1) if

$$\frac{\partial\psi}{\partial t} - \nu K\psi = 0, \quad (2)$$

the "inertia" terms

$$-\frac{\partial\psi}{\partial y} \frac{\partial(\nabla^2\psi)}{\partial x} + \frac{\partial\psi}{\partial x} \frac{\partial(\nabla^2\psi)}{\partial y}$$

vanishing because the stream lines are also lines of constant vorticity. Equation (2) is satisfied if

$$\psi = \psi_1 e^{\nu K t},$$

where  $\psi_1$  is a function of  $x$  and  $y$  only. Hence, if  $\psi_1$  is a solution of

$$\nabla^2\psi_1 = K\psi_1, \quad (3)$$

$$\psi = \psi_1 e^{\nu K t}$$

is a solution of (1).

*Analogy with the theory of vibrating membranes.*

The equation of motion for a vibrating membrane is

$$\nabla^2 z = \frac{1}{c^2} \frac{\partial^2 z}{\partial t^2}, \quad (4)$$

where  $z$  is the displacement at any point from the position

of equilibrium and  $c$  depends only on the tension and mass of the membrane. If the membrane vibrates in simple harmonic motion of period  $T$ , (4) becomes

$$\nabla^2 z + \frac{4\pi^2 z}{c^2 T^2} = 0. \quad (5)$$

This equation is of the same form as (3), and the amplitude of vibration of the membrane may be taken to represent  $\psi$  if

$$K = -4\pi^2/c^2 T^2.$$

It appears therefore that if a solution of the problem of a vibrating membrane has been obtained so that the period and contours, or curves of equal displacement of the membrane, have been determined, a problem of viscous motion has also been solved in which the stream lines are the same as the contours of the vibrating membrane. The velocity of the flow dies down exponentially so that it is reduced in the ratio  $e:1$  in time  $\frac{c^2 T^2}{4\pi^2}$ .

Though the analogy is exact, so far as it goes, it should be borne in mind that in general the boundary conditions in the two cases are different. In the case of a membrane held round its edges, for instance, the boundary condition is  $z=0$ , while for the viscous fluid both  $\psi$  and  $\partial\psi/\partial n$  must be zero at a solid wall. Another point of difference is that if two different solutions have been obtained in the membrane problem, they can be superposed. This is not true in the case of the viscous motion problem because the "inertia" terms in (1), namely,

$$-\frac{\partial\psi}{\partial y} \frac{\partial}{\partial x} (\nabla^2 \psi) + \frac{\partial\psi}{\partial x} \frac{\partial}{\partial y} (\nabla^2 \psi),$$

vanish when  $\psi$  is a solution of

$$\nabla^2 \psi = K_1 \psi, \quad (6)$$

or when it is a solution of

$$\nabla^2 \psi = K_2 \psi, \quad (7)$$

but they do not vanish when  $\psi$  is a sum of solutions of (6) and (7).



*Decay of a system of eddies rotating alternately in opposite directions and arranged in a rectangular array.*

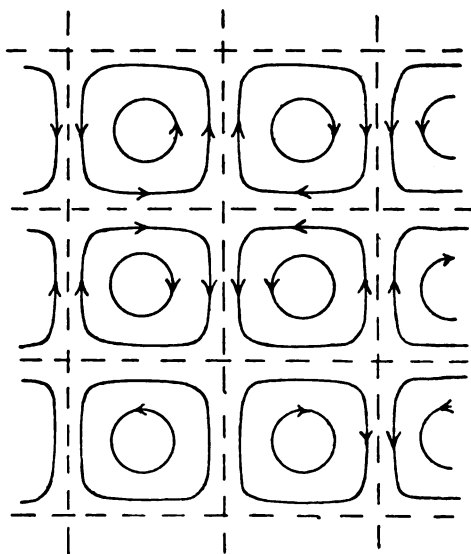
As an example of the use of this type of solution of the equations of motion of a viscous fluid the function

$$\psi_1 = A \cos \frac{\pi x}{d} \cos \frac{\pi y}{d},$$

which is a solution of (3), may be considered. In this case  $K$  is  $2\pi^2/d^2$ , so that the corresponding solution of (1) is

$$\psi = A \cos \frac{\pi x}{d} \cos \frac{\pi y}{d} e^{-\frac{2\pi^2 \nu t}{d^2}}.$$

This represents a system of eddies arranged in a square pattern, each rotating in the opposite direction to that of its four neighbours.  $d$  is the length of the side of a square containing one complete eddy, and such a system is reduced in intensity in the ratio  $e:1$  in time  $d^2/2\pi^2\nu$ . The intensity



Stream lines for system of eddies dying down under the action of viscosity.

of such a system of eddies, each 1 cm. in diameter, for instance, would be reduced to  $1/e$ th in  $\frac{1}{3}$  of a second owing to the action of viscosity if the fluid were air, or  $4\frac{1}{2}$  seconds in the case of water. The stream lines for this system of eddies are shown in the accompanying figure.

LXXVI. *The Period of Protactinium.*By JOHN H. MENNIE, B.A. (*Vanc.*), B.Sc. (*Oxford*) \*.

**P**ROTACTINIUM, the parent of actinium, was discovered by Soddy and Cranston †, and independently by Hahn and Meitner ‡. Shortly after the present investigation was commenced, Hahn and Meitner published an account of a similar research §. Their result has been confirmed by the writer, using a somewhat different method.

Hahn and Meitner separated the protactinium which had formed in a known interval of time in a uranium preparation assumed to be originally free from it, and compared its  $\alpha$ -activity with that of the uranium. They used three separate preparations: 141 grams uranyl nitrate, 20 years old; 86 grams uranyl nitrate, 52 years old; and 33.1 grams sodium uranate plus 21 grams uranyl acetate, 60 years old. The chemical history of these can hardly have been known with absolute accuracy but, as a test experiment with a sample of ordinary commercial uranyl nitrate, freshly prepared, showed practically no protactinium present, they concluded that the ordinary commercial methods of purification are sufficient to remove it all, and hence that their specimens were originally free from protactinium. The uranyl nitrate solution was precipitated with ammonia and the uranium got into solution again by boiling with ammonium carbonate. The precipitate was then dissolved in hydrofluoric acid and a few milligrams of tantalic acid added. The solution was filtered, the filtrate evaporated to dryness, and boiled with aqua regia to remove iron, zirconium, etc., and any traces of uranium and polonium. The tantalum, which was insoluble in the aqua regia, contained the protactinium. This was filtered out and spread on an aluminium plate and its  $\alpha$ -activity compared with that of a known weight of uranium oxide spread on a similar plate. The three results obtained were 12,800, 11,300, and 12,300 years; giving a mean value of 12,000 years for the half-value period.

In the present investigation the period of the protactinium was determined by comparison with that of ionium. The protactinium and also the ionium which had grown in the same time in a uranium preparation originally freed from these elements, were separated and their activities measured.

\* Communicated by Prof. F. Soddy, M.A., F.R.S.

† Proc. Roy. Soc. A, vol. xciv. p. 384 (1918).

‡ *Phys. Zeit.* vol. xiv. p. 208 (1918); vol. xx. p. 127 (1919). *Berichte*, vol. lii. p. 1812 (1919).

§ *Berichte*, vol. liv. p. 69 (1921).

Assuming Hahn and Meitner's value of 3 per cent. for the "branching factor"\* (*i. e.*, the fraction of the uranium atoms which follow the uranium Y actinium mode of disintegration) and 100,000 years as the period of ionium† and neglecting the correction for the difference in range between the two sets of  $\alpha$ -particles, the period of average life of protactinium is given by the following formula in which  $I_{I_0}$  and  $I_{P_a}$  represent the observed activities of the ionium and the protactinium respectively :

$$1/\lambda_{P_a} = \frac{3}{97} \times 100,000 \times \frac{I_{I_0}}{I_{P_a}}.$$

The material used was supplied by Professor Soddy, at whose suggestion this investigation was undertaken. It consisted of a large quantity of uranyl nitrate which had been thoroughly purified in 1909 in the course of work on the radiations of uranium X‡. The period of ionium, already cited, had been obtained by measuring the growth of radium from 6 kilograms of the purest fraction of this uranyl nitrate.

The uranyl nitrate was divided into the several fractions obtained in the last separation of uranium X in September 1909. A portion of the least pure fraction was used in preliminary tests, while the final determinations were made with the "A" fraction. The history of the preparation and the details of the chemical treatment it had undergone were thus very accurately known. It was free from thorium, and it was calculated that the amount of radium and its products which would have been formed in the twelve years since its preparation would not be sufficient to affect the measurements materially. Several kilograms at a time were used, to compensate for the comparatively short time of accumulation of the protactinium.

#### *Methods of Measurement.*

All  $\alpha$ -ray measurements were made with a special electroscope, designed to enable a small  $\alpha$ -radiation to be measured in the presence of an intense  $\beta$ -radiation. This was in order that measurements might be carried out without waiting for the decay of the uranium X which was separated with the ionium. The instrument is a modification

\* *Berichte*, vol. lii. p. 1820 (1919).

† F. Soddy and Miss Hitchins, *Phil. Mag.* (6) vol. xxx. p. 209 (1915);

F. Soddy, *ibid.* (6) vol. xxxviii. p. 483 (1919).

‡ F. Soddy and A. S. Russell, *Phil. Mag.* (6) vol. xviii. p. 620 (1909);

F. Soddy, *Phil. Mag.* (6) vol. xviii. p. 858; vol. xx. p. 343.

of one described by Soddy\*. Its construction is shown in figs. 1 & 2. The body of the electroscope is a brass cylinder about 10 cm. in diameter and 15 cm. in height.

This is made in two parts, to give access to the interior if necessary. They are securely bolted together and the joint is made tight with a leather washer well coated with shellac. (The position of the flange was inadvertently placed too high in the sketch. It must come, of course, below the observation window.) A rubber cork, B, carries the ordinary gold leaf arrangement which is insulated by a sulphur bead C. D is a brass guard-ring and E a wire carrying a piece of watch-spring which may be brought in contact with the gold-leaf system to charge it. The preparation is contained in a small tray, G, about 1 × 6 cm., which slides into a chamber, F, fitted between the poles of a Du Bois electromagnet, with specially shaped pole-pieces K. The chamber ends in a short piece of brass tube, which is closed with a rubber stopper P. The radiation enters the electroscope through a slot, corresponding in size to the tray below it, and covered with a very thin sheet of aluminium foil H (1.4 mg. per sq. cm.). A mica screen, O, of just sufficient thickness (5.5 mg. per sq. cm.) to cut off the  $\alpha$ -rays †, without appreciably affecting the  $\beta$ - and  $\gamma$ -rays, can be moved across the slot by means of a slide, I, operated by a rack and pinion. With the magnet turned on, the greater part of the  $\beta$ -radiation is prevented from entering the electroscope at all, so that the readings are of the order of magnitude of the  $\alpha$ -radiation alone. Simple subtraction of readings taken with and without the mica screen in place give the leak due to the  $\alpha$ -rays. The instrument is filled with hydrogen, and a current of the gas is kept passing through as the readings are made. It enters at L, passes into F through the small openings M (fig. 2), and escapes at N. This has the effect of diminishing the ionization due to the  $\beta$ - and  $\gamma$ -rays, and, at the same time, it intensifies the effect due to the  $\alpha$ -rays, on account of the great increase of their range.

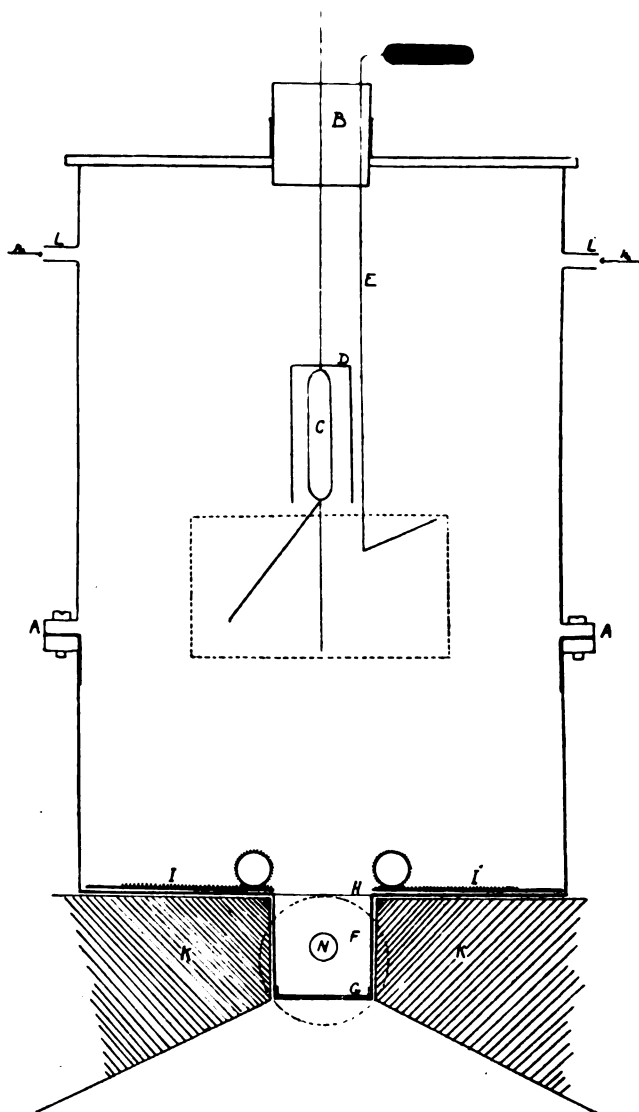
The principal difficulty in making  $\alpha$ -ray measurements is due to the absorption of the radiation by the active material itself. The  $\alpha$ -particles coming from the lower layers of the material are absorbed by the upper layers and consequently the effect observed does not represent the total  $\alpha$ -radiation of the material but only that portion of it which escapes into the electroscope. To overcome this entirely, it would be

\* F. Soddy, *Phil. Mag.* (6) vol. xviii. p. 858 (1909).

† *Annual Reports of the Chem. Soc.* vol. xvii. p. 235 (1920).

necessary to spread the material in an infinitely thin film. Usually an effort is made to approximate to infinite

Fig. 1.

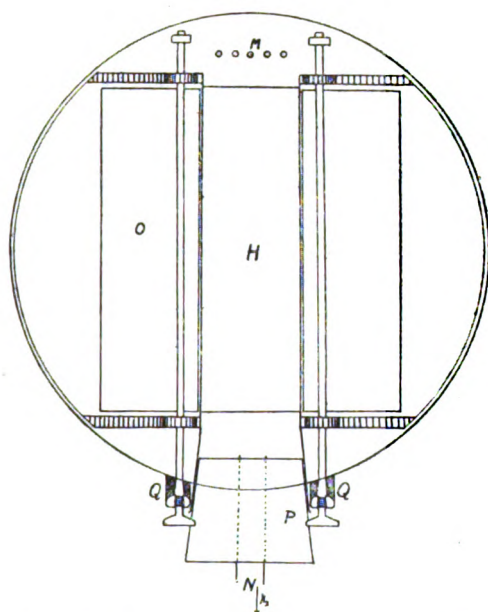


thinness by powdering the material very finely and spreading it on a metal tray or sheet with the aid of some liquid. The

necessity for using a tray of limited area in the magnet electroscop made it necessary to allow for absorption in some other way. The method adopted was based on the following considerations:—

Imagine a layer of radio-active material, one molecule thick. One half of the  $\alpha$ -particles emitted by this layer travel downwards and are absorbed. The other half pass upward into the electroscop and, since there is no absorption by the

Fig. 2.



active material itself, the ionization observed is proportional to the number of  $\alpha$ -particles emitted by the preparation per unit of time. Now, let a second layer be placed on top of the first. The radiation from the lower layer will be partially absorbed in the upper and the effect observed in the electroscop will be, not twice the former value, but somewhat less. As more layers of material are added, the ionization in the electroscop will gradually increase until the thickness of the material is such that the radiation from the bottom layer just fails to penetrate the surface. Further increase in the thickness of the material will cause no change in the ionization produced. This limiting value for the ionization may be called the "surface activity."

Let  $I_0$  be the ionization which would be produced by unit

thickness of a given material if no absorption took place. Then the ionization produced by a layer of infinitesimal thickness,  $dw$ , is  $I_0 dw$ . Let  $s$  be the stopping-power of unit thickness of the material in terms of centimetres of air and let  $W$  be the limiting thickness which is just sufficient to stop the  $\alpha$ -rays from the bottom layer from emerging.

Then  $Ws=R$  or  $W=R/s$ , where  $R$  is the range in air. Let  $I_x$  be the ionization actually produced by a layer of thickness  $dw$ , at depth  $w$  below the surface :

$$\frac{I_x}{I_0 dw} = f(R, ws) * ;$$

therefore

$$I_x = I_0 f(R, ws) dw.$$

The total ionization,  $I$ , produced by a thick layer, is :

$$\begin{aligned} I &= \sum_{x=0}^{x=W} = I_0 \int_0^W f(R, ws) dw \\ &= I_0 \left[ F(R, ws) \right]_0^W \\ &= I_0 \left[ F(R, ws) \right]_0^R \\ &= I_0 \Phi(R). \end{aligned}$$

It follows that for a given type of  $\alpha$ -rays, for which  $R$  is a constant, the observed "surface activity" is directly proportional to the ionization which would be produced by a layer of unit thickness if there were no absorption, *i. e.*, proportional to the number of  $\alpha$ -particles emitted by such a layer per unit of time.

Consider two separate layers of active material of weights  $W'$  and  $W''$  and of unit area. Let their respective "surface activities" be  $I'$  and  $I''$ ; the number of  $\alpha$ -particles emitted per second by the whole layer  $N'$  and  $N''$ ; and the number emitted per second by a layer of unit thickness,  $n'$  and  $n''$ . It has just been shown that  $n' = kI'$  and  $n'' = kI''$  ( $k$ =a constant).

$$\begin{aligned} N' &= W' n' = W' k I', \\ N'' &= W'' n'' = W'' k I''; \quad \text{therefore} \quad \frac{N'}{N''} = \frac{W' I'}{W'' I''}. \end{aligned}$$

This was the principle of the method of measurement

\* Rutherford, 'Radio-active Substances and their Radiations,' p. 160. Rutherford states: "... the total ionization due to thick layers of radio-active matter of different kinds is approximately proportional to  $R^2$ , where  $R$  is the range of the  $\alpha$ -particles emitted."

employed. The preparations were of more than the limiting thickness, so that the activity measured in each case was the "surface activity." This, in arbitrary units (the rate of leak of the electroscope in scale divisions per minute), was multiplied by the weight of the preparation and the figure so obtained was taken as proportional to the total activity of the material, *i. e.*, the entire number of  $\alpha$ -particles given out per second. An effort was made to have the preparations which were compared as nearly alike as possible, both in weight and composition.

### *The Chemical Separations.*

As ionium is isotopic with uranium X, any chemical method of separating the one applies equally to the other. Owing to the high degree of purity of the uranyl nitrate many of the ordinary methods for separating uranium X failed. The method finally adopted was as follows:—The uranyl nitrate was treated by extraction with ether\*. The final water layer was evaporated to dryness, ignited carefully to uranic oxide,  $\text{UO}_3$ , and dissolved in hydrofluoric acid. A very small amount of insoluble residue contained the greater part of the ionium and uranium X. (A satisfactory separation by simple precipitation with hydrofluoric acid could not be obtained. The fluorides of cerium, thorium, etc., are quite soluble in solutions of uranium salts such as uranyl nitrate. The ordinary black oxide of uranium,  $\text{U}_3\text{O}_8$ , refuses to go into solution in hydrofluoric acid, but uranic oxide,  $\text{UO}_3$ , dissolves quite readily, leaving the insoluble fluorides behind.) The separation of ionium by this method was not absolutely complete but its extent could be determined by  $\beta$ -ray measurements of the uranium X. The exact proportion of the total ionium present in any preparation could in this way be readily calculated.

When the uranyl nitrate was first brought into solution, it was found to contain a certain amount of dust and dirt. It was thought possible that this might have carried down with it some of the protactinium, which may be expected to share the excessive insolubility of its analogue, tantalum. The dust was filtered out and boiled with hydrofluoric acid, the extract being added to the above hydrofluoric acid solution. The latter was then poured into ammonium carbonate solution to get rid of the uranium. To the resulting precipitate, after ignition and boiling with nitric acid, was added the residue

\* Soddy, 'The Chemistry of the Radio-Elements,' p. 38.



from the extraction of the dust. The whole was then spread on a platinum tray and its  $\alpha$ -radiation measured. It contained the whole of the protactinium present, with a small amount of ionium which was estimated from the isotopic uranium X present by  $\beta$ -ray measurements.

The fluoride precipitate containing the greater part of the ionium was then added to it, the two were thoroughly mixed and the  $\alpha$ -ray measurements repeated. The expedient of mixing the two, rather than measuring them separately, was adopted on account of the very small amount of the fluoride residue, in order that the preparations compared should be as nearly as possible of the same composition.

The method of calculation is illustrated by the following, which gives the result of this determination :—

Weight of uranyl nitrate used :		4.780 kgm.
	Pa.	Pa + Io.
Weight of preparation .....	0.0804	0.0912 gm.
$\alpha$ -activity .....	5.55	15.78
$\beta$ -activity .....	9.03	70.91
$\beta$ -ray measurements showed the fluoride residue to contain 40 per cent. of the original ionium present in the uranium.		
$\beta$ -activity of (40 + X) per cent. Io	=	70.91
„ X per cent. Io	=	9.03
„ 40 per cent. Io	=	61.88
therefore $X = 9.03 / 61.88 \times 40 = 5.8$ per cent.		
$\alpha$ -activity of 45.8 per cent. Io + Pa =	$15.78 \times 0.0912 =$	1.4391
„ 5.8 per cent. Io + Pa =	$5.55 \times 0.0804 =$	.4662
„ 40 per cent. Io	=	.9729
„ 5.8 per cent. Io	=	.1431
„ total Io	=	2.4322
„ Pa =	.4662 - .1431	= .3231
therefore $1/\lambda_{Pa} = \frac{3}{97} \times 100,000 \times \frac{2.4322}{.3231} = 23,300$ years.		

A previous determination was carried out in a similar manner but the activity of the residue from the hydrofluoric acid extraction of the dust was measured separately. The result obtained was 15,500 years.

In the preliminary experiments on “D” fraction of the material, the chemical methods used were quite different. After repeated fractional crystallization of the uranyl nitrate, the mother liquor was poured into dilute ammonium carbonate

solution. The precipitate carries down with it the radioactive elements present in minute quantity in the uranium \*. This process of crystallization was repeated several times till the last precipitate showed a negligible  $\alpha$ -activity. After  $\alpha$ -ray measurements on the total ammonium carbonate precipitate (Pa + Io), it was dissolved in nitric acid, and the protactinium removed by shaking with successive small portions of tantalic acid † until the last of these showed a negligible  $\alpha$ -activity. These were then combined and their total activity measured.

The first rough trial on one kilogram of material gave a figure of 28,800 years for the period; a second and more careful application of the method on two kilograms of material gave 16,000 years.

The same method was then applied to a portion of the "A" fraction of the uranyl nitrate. This was so free from impurities that only a faint precipitate was obtained with ammonium carbonate, which gave only a very slight separation of the ionium. The ether and fluoride separation, already described, was then applied. In this case, the ionium fluoride was not combined with the protactinium preparation but was measured separately, a little tantalic acid being added to it to make the weights of the two preparations approximately alike. The period was calculated to be 17,300 years.

In all cases, the behaviour of the ionium at all stages of the treatment could be followed and the proportion present in any preparation ascertained by measurements of the  $\beta$ - or  $\gamma$ -radiation of its isotope, uranium X. Efforts were directed, therefore, to obtaining an accurately known portion of the ionium present for measurement, rather than the whole. Unfortunately, no similar means of tracing the protactinium were available. It was assumed to follow the behaviour which might be expected of it as an analogue of tantalum. Evidence that this is justified is provided by the fact that the result of the second experiment is in good agreement with the later ones, and in this earlier method the completeness of the separation of the protactinium and the ionium from the uranium and from each other was tested by repeating the process of separation and testing each successive product until it ceased to give a measurable  $\alpha$ -radiation. If the removal of the protactinium was in any

\* Soddy, 'The Chemistry of the Radio-Elements,' p. 38.

† Hahn and Meitner, *Phys. Zeit.* vol. xiv. p. 758 (1913).

case incomplete, then the value calculated for the period is a maximum one.

In the calculations, the difference in range between the  $\alpha$ -particles of ionium and protactinium has not been taken into account. The ranges are close together (3.1 and 3.5 cm.) so that the correction would in any case be small, probably not larger than the experimental error.

### Results.

The results obtained may be tabulated as follows :—

Material.	Weight (in kgs.).	Chemical treatment.	Average Life Period of Pa.
"D" .....	1	Crystallization and ammonium carbonate.	(28,200) yrs.
"D" .....	2	Do.	16,000 "
"A" .....	2.5	Crystallization and ammonium carbonate followed by ether and fluoride.	17,300 "
"A" .....	4.197	Ether and fluoride.	15,500 "
"A" .....	4.780	Do.	23,300 "

Mean ..... 18,000 yrs.

The agreement among the individual values is reasonably satisfactory, especially in view of the very considerable alterations in the procedure between the separate determinations. Neglecting the first, which was merely a rough trial of the method, the mean is 18,000 years, which corresponds to a half-value period of 12,500 years. This closely confirms Hahn and Meitner's conclusion.

The period was also calculated by comparing the activity of the protactinium with that of uranium. The formula used was  $1/\lambda_{Pa} = \frac{\frac{1}{2}I_u}{I_{Pa}} \times 0.03t$ , where  $t$  is the time from purification in years.

The values used for  $I_u$  and  $I_{Pa}$  were, of course, weight times activity; in the case of the uranium, the weight taken being the weight of uranium oxide equivalent to the entire amount of uranyl nitrate from which the protactinium had been separated.

The results obtained were:—23,700 ; 26,400 ; 9,500 ; 20,800. Neglecting the third, which for some reason displays a wide discrepancy from the others, the mean is 23,600, which corresponds to a half-value period of 16,400.

Exactly the same method of calculation may be used to arrive at the period of ionium. The results found were:—149,000 ; 153,000 ; 62,000 ; 79,200. While the mean of these is not far from 100,000, they differ too widely among themselves for any reliance to be placed upon them. This fact casts some doubt on the reliability of the calculations of the period of protactinium from comparison with uranium, and the value obtained by the comparison with ionium is probably more certain.

The foregoing is based on the usual assumption that protactinium is the product of the short-lived uranium Y. If, as Dr. A. S. Russell has suggested in a recent letter to 'Nature'\*, the parent of protactinium is not uranium Y, but an unknown element of comparatively long period, the value here found for the period of protactinium is a maximum, and must be reduced to an extent depending on the period of its parent.

In conclusion, I wish to express my very grateful acknowledgement to Professor Soddy for his invaluable advice and suggestions, and for supplying the unique uranium preparation which made this work possible.

#### *Summary.*

The period of protactinium has been estimated from a comparison of the  $\alpha$ -activities of the ionium and protactinium separated from a large quantity of uranium purified in 1909 by Professor Soddy. The mean value obtained is 18,000 years for the period of average life, which is in substantial agreement with the period of half-change, 12,500 years, obtained by Hahn and Meitner.

Old Chemistry Department,  
University Museum, Oxford.

\* 'Nature,' vol. iii. p. 703 (May 26th, 1923).

**LXXVII. Forced Oscillations in Self-maintained Oscillating Circuits.** (*Thesis accepted for the Degree of Ph.D. in the University of London* \*.) By W. A. LEYSHON, B.Sc.†

CONTENTS.

Section 1. Introductory.

- „ 2. Apparatus.
- „ 3. Description of Lissajous' instrument.
- „ 4. Test of Lissajous' instrument as an indicator of phase difference.
- „ 5. Experimental results obtained.
- „ 6. Notes on the results obtained.

SECTION 1.—*Introductory.*

**T**HE present paper is concerned with the behaviour of certain electrical circuits maintained in oscillation by a three-electrode thermionic tube, or triode, under the influence of impressed oscillations.

If two inductance-capacity valve-maintained oscillating circuits are closely coupled, and in tune, it is well known that the capacity of the condenser in either circuit can be varied within comparatively wide limits without the phenomenon of beats occurring. The circuits seem to pull each other into tune, even when their proper frequencies (if uncoupled) differ considerably. The extent to which this “pulling into tune” occurs increases with the coupling.

Some experiments by Vincent suggested that the phase difference between the oscillating currents in the two circuits changed from  $0^\circ$  to  $180^\circ$  (or *vice versa*) as the capacity of the condenser in one circuit was varied. Two circuits which are mutually held in this way at the same frequency, although not necessarily in phase, may be said to be in the “accordant state.”

In the experiments to be described an alternating voltage was applied to an oscillating triode system, either by means

\* A paper by Dr. E. V. Appleton on “The Automatic Synchronization of Triode Oscillators” appeared in the Proceedings of the Cambridge Philosophical Society, vol. xxi. pt. 3, Nov. 14, 1922, at the moment the writing of this thesis was approaching completion. Dr. Appleton attacks a problem similar to that of the present writer by an entirely different method.

† Communicated by Prof. W. H. Eccles, F.R.S.

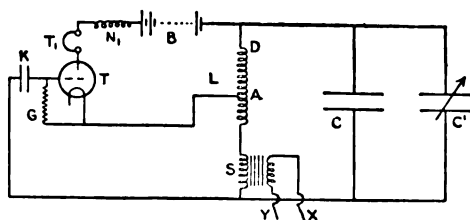
of a second triode system, which was itself acted on by the first system, or by means of a circuit (possessing constant amplitude and frequency) maintained by a tuning-fork and two triodes in parallel.

Low frequency oscillating circuits were employed and the phase differences it was desired to observe were shown by means of a Lissajous instrument designed for the purpose which is described in Section 3.

## SECTION 2.—*Apparatus.*

Experiments were made with circuits arranged as in fig. 1

Fig. 1.



$N_1$  = coils of Lissajous' instrument.

$T_1$  = telephones.

$T$  = triode ("R" pattern).

$K$  = grid condenser (.02 microfarad).

$G$  = grid leak (ca. 1 megohm).

$L$  = inductance.

$C$  = bank of condensers or fixed condenser.

$C'$  = variable air-condenser.

$S$  = coupling coil.

$X, Y$  = points connected to second oscillatory circuit.

In fig. 1 the condensers ( $C$ ) and  $C'$  are shown in shunt to the whole inductance  $L$  and coupling coil  $S$ . In some experiments they were in parallel with  $DA$  only.

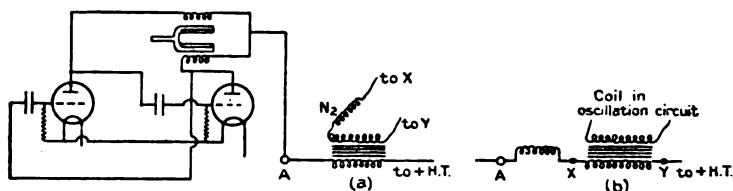
In some experiments  $S$  consisted of two three-layered solenoids which could be adjusted in position on a common iron core ("weak" coupling); in others, of two or four "bisenit coils" wound on a laminated stalloy core, and having a much greater mutual inductance than that of the solenoids ("strong" coupling).

The points  $X, Y$  were connected either to a circuit similar to that shown in fig. 1, or to a circuit in which oscillations of constant frequency and amplitude were maintained by

means of a tuning-fork set \*. This is shown in fig. 2, in which (a) shows the circuit coupled to the tuning-fork set in which X, Y are connected, and (b) shows one coil of S included in the battery circuit of the tuning-fork set.

Two tuning-forks were used, one having a frequency of 450, and the other of 256.

Fig. 2.



The inductance-capacity circuits were tuned, first by adjusting the capacity  $C$  (fig. 1), then by adjusting the filament temperature of the triode, then by adjusting the voltage applied to the triode, and finally by means of the variable air-condensers in parallel with  $C$ .

In the experiments to be described, the circuits were usually so coupled that the accordant state persisted over a limited range of alteration of the capacity of  $C'$  (fig. 1).

The phase relations between corresponding currents in the two coupled circuits were observed by means of the instrument described in the next section.

### SECTION 3.—*The Lissajous instrument.*

This consisted of a very fine magnetized steel needle, with the eye removed, which was kept in vibration by means of two perpendicular pairs of coils, through which the respective alternating currents were passed. The vibrations of the needle were observed by means of a microscope.

The needles used were "superfine beading" needles, which are longer and finer than the finest sewing needles manufactured. The average diameter was about 14 mils. In cutting the needle to the desired length, the inner crystalline structure was exposed, so that when the light of an electric lamp was focussed on to the cut surface, a number of brilliant points of light were seen through the microscope. The figures described by these points of light could be very clearly seen in the course of the experiments. The needle used for any particular experiment had a natural frequency

\* Eccles & Jordan, "Sustaining the Vibration of a Tuning-fork by a Triode Valve," *Electrician*, June 20, 1919. "A Method of using two Triode Valves in parallel for generating Oscillations" (Paper read before B.A. (Eng.) Meeting, 1919).

not very different from that of the electrical circuits whose oscillations caused it to be set in vibration.

In the first form of the apparatus, the point of the needle was pushed into a cylinder of wood which fitted into a vertical hole in a block of wood placed on the stage of the microscope. Horizontal grooves in this block carried the exciting coils, whose positions could be adjusted slightly by means of small wedges placed on either side of each coil and between the coil and the walls of the groove.

In a later form, the wooden cylinder carrying the needle was a short piece of hard wood (actually a piece of a penholder) which fitted tightly into a brass tube. The brass tube could be screwed through a hole in a brass plate, and was kept in position by a nut.

The brass plate, which rested on the stage of the microscope, supported by means of three pillars a shallow square brass box, into which a square block of wood fitted.

The exciting coils were fitted in horizontal grooves in this block, their positions being slightly adjustable as before. Figs. 3 and 4 show the arrangement of the apparatus, fig. 4 showing the needle in position in the holder.

The exciting coils were Brown 4000 ohm A type telephone coils, which had been modified as suggested in figs. 5 (a) and (b). The pole-pieces AB were filed down to

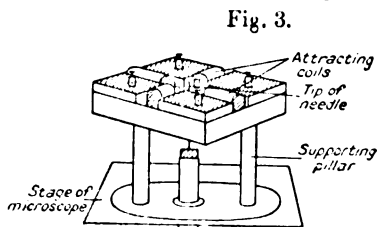


Fig. 3.

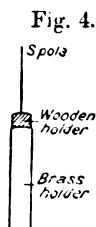


Fig. 4.

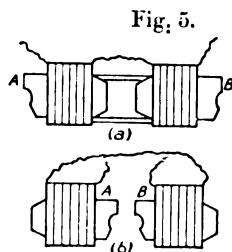


Fig. 5.

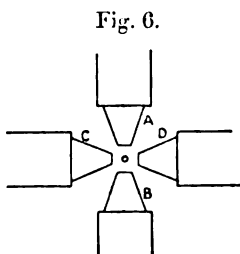


Fig. 6.

a thickness of 1 mm. at the ends, so that they could be brought within a small distance of the upper end of the needle.

Fig. 6 shows the arrangement of the exciting coils and needle as seen from above.



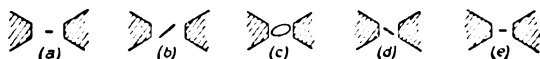
The eyepiece of the microscope finally used was fitted with a micrometer marked out in  $\frac{1}{4}$ -mm. squares, so that it could readily be verified that the straight lines seen when the coils AB alone were in action were in the direction AB, and accurately perpendicular to the straight lines seen when the coils CD were in action alone.

With both coils in action and currents of the same frequency passing through them, the Lissajous figure corresponding to the difference of phase between the currents was seen.

When the currents differed in frequency, the changing figures during the beats could be observed with ease.

It was found advisable not to work too near the tune of the needle. At this point the amplitude of oscillation increased to a great extent, and if one set of coils only were in action, the figures seen as the exciting current passed through the natural frequency of the needle were as shown in fig. 7.

Fig. 7.



The figures are probably due to the difference in proper frequency of the needle in the two perpendicular directions, a small oscillation in the  $\uparrow$  direction being maintained near the tuning point. It should be noted that the changes (a) to (e) occurred for quite small variations in frequency, particularly when a needle of almost circular section (as seen under a microscope magnifying a hundred times) was used.

The following considerations also indicate that it is better to use a mistuned needle :—

Suppose the amplitude of oscillation small (which it was in all the cases considered).

Let  $p_1$  = period of (undamped) needle in one direction.

Let  $p_2$  = period of (undamped) needle in the perpendicular direction.

$$\text{Then} \quad \tan \delta_1 = \frac{2k_1 n}{p_1^2 - n^2},$$

where  $k$  = damping factor,

$n$  = frequency of impressed force,

$\delta_1$  = phase angle between displacement and impressed force.

Similarly  $\tan \delta_2 = \frac{2k_2 n}{p_2^2 - n^2}.$

Provided  $k_1 \approx k_2$  and  $n$  differs considerably from  $p_1$  and  $p_2$ , the needle shows very approximately the phase difference between the impressed forces.

But if  $n$  is very nearly equal to  $p_1$  and  $p_1 \neq p_2$ , there may be a considerable error due to the difference between  $\delta_1$  and  $\delta_2$ .

To calculate the length of the needle required for a particular frequency, the formula  $N_1 = \frac{0.525kb^*}{l^2}$  may be used,

where  $N_1$  = frequency,

$k$  = radius of gyration of cross-section about axis

$\left(\frac{r}{2} \text{ for cylindrical rod radius } r\right),$

$q$  = Young's modulus,

$\rho$  = density,

$l$  = length,

$$b = \sqrt{\frac{q}{\rho}}.$$

If  $N = (\text{say}) 50,$

$$\rho = 7.8,$$

$$q = 20.9 \times 10^{11}, \text{ this gives } \frac{r}{l^2} = 0.000368.$$

For the needles used,  $r \approx 0.015$  ;

$$\therefore l = 5 \sqrt{\frac{0.015}{0.000368}},$$

$$= 6.4 \text{ cm.}$$

In an actual experiment it was found that for  $l = 5 \text{ cm.},$   
 $N \approx 85.$

Therefore for  $N = 50,$

$$l = \sqrt{\frac{85}{50}},$$

$$= 6.5 \text{ cm.}$$

\* Barton, 'Theory of Sound,' p. 292.

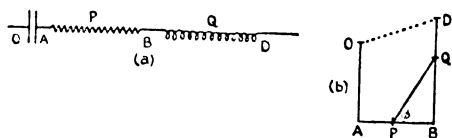
SECTION 4.—*Experiments to test the Lissajous instrument as an indicator of phase difference between the currents in the pairs of coils.*

Suppose an alternating current sent through a circuit consisting of a condenser, a resistance, and an inductance in series\*.

The variations of the P.D. between O and D with time can be represented in the well-known way by an Argand diagram. If the variations in the P.D. between O and A and between B and D with time are represented similarly in the same diagram, the radius vector representing the P.D. between O and A will be  $90^\circ$  behind that representing P.D. between A and B, and that representing the P.D. between B and D will be  $90^\circ$  ahead of the resistance radius vector.

The direction in the Argand diagram of the radius vector representing the P.D. between O and D is found, as shown in fig. 8, by the dotted line OD.

Fig. 8.



Similarly the line PQ gives the direction and length of the radius vector representing the P.D. between the points P and Q, the direction of the resistance radius vector being given by AB.

If the points O and A are connected by a resistance of such value that the current flowing in this shunt circuit is negligible in comparison with that flowing through the main circuit, then this current will be in phase with the P.D. across the condenser, and therefore  $90^\circ$  out of phase with the current in OABD.

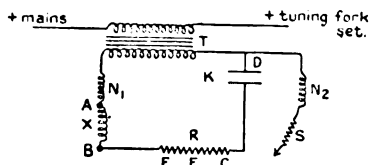
As indicated in fig. 8 (b), the current in such a shunt across PQ would make an angle of  $\phi^\circ$  with the main current.

The apparatus used in the tests to be described is indicated in fig. 9.

\* Eccles, 'Continuous Wave Wireless Telegraphy,' p. 139.

The results obtained are given in Table I. It should be noted that the impedance of the coils  $N_1$ ,  $N_2$  is practically resistive at frequency 256.

Fig. 9.



T=iron-cored transformer, the primary of which was included in the battery circuit of the T.F. set.

K=condenser.

L=inductance.

R=resistance.

$N_1$ ,  $N_2$ =coils of Lissajous instrument.

S=resistance in series with  $N_2$ .

In some experiments  $N_1$  was placed in shunt to some part of the circuit.

TABLE I.

Position of $N_1$ .	Position of $N_2$ .	Figures seen.	Notes.
1. In the oscillation circuit.	DC	O, provided condenser was sufficiently large.	
2. " "	In    with $N_1$ .	\ [in phase].	Using a needle more nearly tuned to 256, figure seen was O.
3. Across DC with about 10,000 ohms in series.	AX	/ [out of phase].	
4. In the oscillation circuit.	AX	O	
5. BF	DE	O $\rightarrow$ O	As part of R in series with condenser was increased.

From these and similar experiments, it was concluded that a distuned needle could be relied on as an indicator of phase difference.

SECTION 5.—*Experimental results obtained with two coupled oscillating circuits.*

## 1. Lissajous' figures seen in the accordant state.

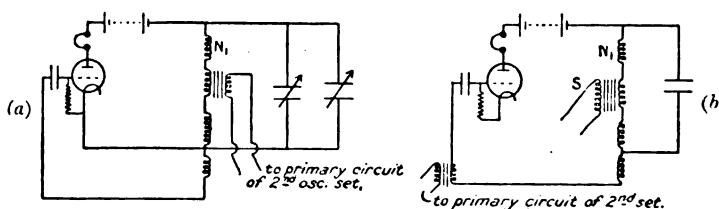
## (a) Two inductance-capacity oscillating sets.

Some typical results are shown in Table II.

As already stated, the first experiments made were with the apparatus of fig. 1.

Other experiments have been made with the circuits shown in fig. 10.

Fig. 10.



In making the first sets of observations (1 in Table II.), it was observed that the same figures were obtained in the same order when, instead of increasing the capacity of the variable condenser in Set 1, the capacity of the variable condenser in Set 2 was diminished.

It was also observed that with sufficiently strong coupling between the circuits, the same figure was seen for the same setting of the variable condenser, whether the setting were approached from a larger or a smaller value.

This was not the case with weaker coupling—the same figure was seen for a higher condenser reading when the accordant state was reached by increasing the capacity of the tuning condenser than when it was reached by diminishing the capacity.

It was found on diminishing the coupling between the oscillating circuits, these being otherwise left unchanged, that provided the change in coupling were not too great, the same figures were seen, but the range of capacity over which the accordant state was observable diminished with the coupling.

The observations referred to in 1 (Table II.) were made with different needles—to suit the different frequencies employed.

TABLE II.

Circuits.	Coupling.	Figures seen.	Frequency.	Notes.
1. As fig. 1.	Strong or weak.	Set 1 condenser increasing $\rightarrow$ $\diagup O \diagdown$	85-150	In these first observations it is not certain which is the in-phase figure.
2. As fig. 1. but needle coils in oscillation circuit.	Strong -	$\diagup O \diagdown \emptyset$	ca. 256	$\diagdown$ is the in-phase condition.
3. As fig. 1.	Strong.	$\emptyset O \diagdown \emptyset$	"	"
4. Fig. 10(a).	Weak.	$\diagdown O \diagup$	"	Apparently, but very small range of accordant state. Both sets oscillating strongly.
5. "	Fairly strong +	$\emptyset \diagup O \diagdown$	"	$\diagdown$ is the in-phase condition.
6. "	" -	$\emptyset \diagdown O \emptyset$	"	"
7. "	Strong + " -	$\emptyset$ $\emptyset$	"	This figure was seen over whole range of capacity of tuning condenser.
8. Fig. 10(b).	"	$O \diagup O$	"	$\diagdown$ is the in-phase condition.

Those referred to in 2-7 were made with one of the needles which were fitted in turn in the apparatus when this was tested as a measurer of phase difference.

With conditions as in 3, Table II., and the figure  $\emptyset$  showing, stopping Set 2 (by breaking the filament or battery circuit) caused the note of Set 1 to be raised appreciably in pitch.

With conditions as in 7, Table II., and figure  $\bigcirc$  (Set 1 condenser large), stopping Set 2 (as above) lowered the frequency of Set 1, and stopping Set 1 raised the frequency of Set 2.

The accordant state figures have been observed, using one set an octave above the other\*; the tuning was very sharp, even with strong coupling. This case has not been further investigated.

\* Cf. "Sur la synchronisation harmonique des oscillations électriques." Mercier, *Comptes Rendus*, clxiv. pp. 448-450, Feb. 13, 1922.

It should be observed that in all the arrangements used (except that of fig. 10, *a*), each oscillating set caused a straight-line oscillation of the needle between the coils connected in that set when the filament or anode battery circuit of the other set was broken.

In the case of the arrangement used in fig. 10 (*a*), this was not so.

Accordant state figures have been seen using the circuit of fig. 1, except that the grids of the two oscillating sets were connected through a condenser, no coupling transformer being used in the circuits.

1 (*b*). Lissajous' figures seen in the accordant state—using a tuning-fork set and an inductance-capacity set:—

The results given in Table III. were obtained, using the circuits of fig. 2 (*a*) and (*b*), and of figs. 1 and 10 (*b*) (coupling coils S omitted).

TABLE III.

	Circuits.	Coupling.	Figures seen.	Frequency.	Notes.
1.	Figs. 1 & 2 ( <i>b</i> ).	Strong. T.F. set oscillating strongly.	Set 1 condenser increasing $\rightarrow$ O /	450 & 256	Not known which is the in-phase condition.
2.	"	Strong. Inductance capacity set oscillating very strongly—or amplitude of T.F. set not very great.	\ O jerked to /	"	...
3.	Figs. 10 ( <i>b</i> ) & 3 ( <i>a</i> ).	Fairly strong + " -	O \ jerked to O $\theta$ O jerk $\theta$ / O	...	...
4.	"	Strong +	$\infty$ \ O	...	\ in-phase.
5.	"	" -	O /	...	...

+ coupling in the above Table means that when the currents in the circuit containing the primary of the coupling coil, and in the oscillating circuit were in phase, the grid voltage and what may be termed the "accordant voltage" were also in phase.

Under conditions 1 and 2 of Table III., it was found that the range of capacity of the tuning condenser covering the accordant state was diminished with diminished amplitude of the tuning-fork set.

With "weak" coupling very complicated figures were

sometimes obtained, one figure changing abruptly to another as the tuning condenser was varied steadily.

With a crystal detector and galvanometer across this tuning condenser (and a high resistance in series with these), the sudden changes of figure were seen to be accompanied by sudden slight changes in the current through the galvanometer.

With conditions as in 4, Table III., breaking the filament circuit of the tuning-fork set so as to stop the vibration of the fork (figure  $\bigcirc$  showing) lowered the frequency of Set 1. With the figure  $\oslash$  showing, breaking the filament circuit of the tuning-fork set raised the frequency of Set 1 slightly.

With conditions as in 5, Table III., breaking the T.F. set filament circuit lowered the frequency when figure  $\bigcirc$  was showing.

With conditions as above, reducing the amplitude of oscillation of the tuning-fork circuit by lowering the filament current caused the figure to change to  $\bigcirc$ , and finally to  $\searrow$  just before the oscillations of the T.F. set died away. (This apparently corresponds to 2, Table III.)

## 2. Lissajous' figures observed during beats :—

Provided that the coupling between the two oscillating circuits was not too strong, so that the beat frequency was not too great when the accordant state had just been upset, it was possible to watch the phase changes during the beating process.

These phase changes were found to occur uniformly with time (*i. e.* the change from one figure to another, representing a change of phase difference  $\phi$ , took the same fraction of a whole beat period whatever the first figure observed) when there was no coupling between the circuits. It was found impossible, with the tuning condensers used, to bring the circuits exactly into tune with this arrangement.

With coupling between the oscillating circuits, the phase changes did not occur uniformly with time during the beats. Using the circuits and conditions of Tables II. and III. (1), it was observed that the non-uniform phase changes during beats were different on the two sides of the accordant state—*i. e.*, for the higher and lower settings of the tuning condenser.

It was observed that the figure last seen in the accordant state before beating began was the figure longest in view during the beat.

With loose coupling between the tuning-fork set and an inductance-capacity set (when the figures changed by jerks



in the accordant state), the figures seemed to go through a kind of drill when beating began.

Increasing the coupling between the two oscillating circuits intensified the non-uniformity of the beats; with sufficiently strong coupling between the circuits, changes of frequency corresponding to the changes of figure could be heard in the telephones in the oscillating circuit.

#### SECTION 6.—*Notes on the results obtained.*

The foregoing experiments on the accordant state suggest generally that when an alternating voltage of constant frequency and amplitude is applied to the grid of an oscillating triode, this voltage not differing markedly in frequency from that of the undisturbed oscillating system, the latter may be pulled into tune with the according voltage if the latter is sufficiently great. The phase difference between the grid voltage as supplied by the oscillating triode and the according voltage in the accordant state depends on the strength of the latter, and on the difference in the frequency of the system supplying the according voltage and the undisturbed frequency of the triode system.

When the according voltage is not sufficiently strong to pull the triode system into tune, modified beats are observed, the rate of change of phase with time being least when the phase difference is such that the triode system is most nearly in tune with the applied voltage.

In the experimental results obtained, only one-quarter of a cycle of phase change has been observed in the accordant state with comparatively strong according voltages.

When an alternating voltage supplied by a triode system is applied to a second triode system, which itself affects the first system, half a cycle of phase change has been observed to take place between corresponding currents in the two triode systems.

In conclusion, my thanks are due to Professor W. H. Eccles, F.R.S., for suggesting the problem and the method of investigating it, for the loan of much apparatus, and for his help and advice; also to Dr. J. G. Barns for the use of his microscope; and to my father, Mr. R. Leyshon, for his help in developing the Lissajous instrument during the summer vacation.

November 1922.

LXXVIII. *A Statistical Investigation of the Visibility of Red Light.* By R. A. HOUSTOUN, Ph.D., D.Sc., Lecturer on Physical Optics in the University of Glasgow, and ERIC W. M. HEDDLE, M.A., B.Sc., Lecturer in Mathematics in the Royal Technical College, Glasgow\*.

**D**URING the past six years or so a statistical survey of the colour vision of some two thousand students has been carried out at the University of Glasgow. This survey has shown that some observers have better colour vision than the average and some worse, following the law of normal deviation, and that normal deviation almost covers everything so far as women are concerned. In the case of men, however, the colour blind and red and green anomalies occur scattered outside the normal curve.

Some observers see the red end of the spectrum much dimmer than others. The object of the present investigation was to see whether these observers were an extreme case of normal variation or not, and also to find to what extent they occurred. The investigation has also a bearing on the original Young-Helmholtz theory of colour vision, according to which the colour blind were divided into two well-defined classes, the red blind and the green blind, a view which Helmholtz himself afterwards abandoned.

§ 1. We find the most valuable previous data on the subject in a paper by Coblentz and Emerson†. By means of a flicker photometer they determined the relative visibility of the different colours of the spectrum for 125 different observers who were apparently a random distribution so far as colour vision is concerned; their results are exhibited in a table. The wave-length  $665\text{ }\mu\mu$  is the point nearest the red end of the spectrum for which every one of the 125 observers made a reading. The table gives the ratio of the visibility of this colour to the visibility of the most visible colour in the spectrum for each of the observers. The results vary from .252 to .822. The most visible colour in the spectrum is always in the green, though its position varies somewhat from one observer to another. The two numbers cited above, therefore, give the ratio of the brightness of the red to the brightness of the green, multiplied by a constant factor, for the two observers in question. If the logarithm of this ratio is taken, the 125 observers can be

\* Communicated by the Authors.

† "Relative Sensibility of the Average Eye to Light of Different Colours and Some Practical Applications to Radiation Problems," Bull. Bur. Standards, xiv. p. 167 (1918).

grouped in the following manner in terms of its value ; in the table the characteristic of the logarithm is omitted :—

Logarithm.	No. of Observers.	Logarithm.	No. of Observers.
·40 & < ·44	2	·68 & < ·72	19
·44 & < ·48	0	·72 & < ·76	18
·48 & < ·52	3	·76 & < ·80	11
·52 & < ·56	8	·80 & < ·84	7
·56 & < ·60	10	·84 & < ·88	2
·60 & < ·64	18	·88 & < ·92	1
·64 & < ·68	26		

The table is plotted in fig. 2. The number of observers is grouped against logarithm of ratio instead of against ratio for a reason that will be explained later in connexion with our own results. The distribution represented in fig. 2 is not far off the normal curve. Coblentz and Emerson subdivide their observers into various groups for convenience of handling, red sensitive, blue sensitive, &c., but these groups are arbitrary. There is nothing in the paper to show that we are not dealing with one homogeneous population.

§2. As we desired only to get one reading for each observer, the arrangement of Coblentz and Emerson would have been too elaborate for our purpose. We made three false starts before obtaining an apparatus to our taste.

(1) First of all an attempt was made with a specially-fitted spectroscope to put the cross-wire on the red end of a continuous spectrum. We had never much hope of this method, and it failed owing to diffuse light in the instrument and variation of the reading with the state of dark adaptation of the observer's eye.

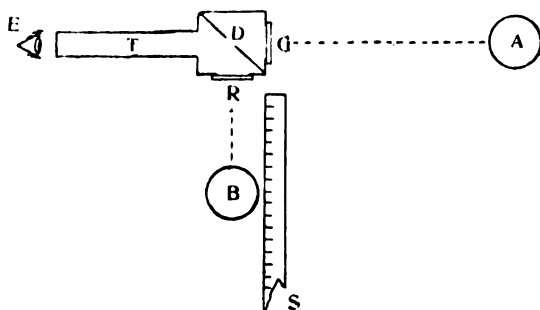
(2) A thin piece of copper with two very fine holes drilled in it was placed on the stage of a low-power microscope. Behind one of these holes was a piece of red glass; behind the other a wedge of neutral glass. On looking into the microscope the observer saw a red disk, something like a signal lamp at a hundred yards or so, and a grey disk beside it. By rotating a wheel which carried the wedge he adjusted the luminosity of the grey disk, until the two disks were equally bright. This method was abandoned, because the

"neutral" wedge had a green tint, because the range of adjustment was not great enough, and because a slight displacement of the piece of copper on which the holes were drilled had a great influence on the result.

(3) We next measured a red light against a white one by means of a Simmance-Abady flicker photometer. But the fact that this instrument gives more consistent readings than the grease-spot or shadow photometers when the colours are different was outweighed by its inconvenience and unfamiliarity to the observers. So it was abandoned in favour of the simple arrangement of the grease-spot type the plan of which is shown in fig. 1.

T is a tube about 18 cm. long and of 2.5 cm. diameter, with a small hole at the end of 4 mm. diameter into which the eye E of the observer looks. He sees a diamond shaped

Fig. 1.



opening D of 8 mm. side in a piece of paper which is stretched diagonally across a cubical box of 5 cm. side. Through this opening a ground-glass plate G is visible; this plate is illuminated by an 8 candle-power carbon glow-lamp A at a fixed distance of 2 metres. Light from a 16 candle-power carbon glow-lamp B falls on the front of the paper through the piece of clear red glass R. Consequently the observer sees a white diamond against a red background. The lamp B moves along a scale S 50 cm. long, and its position on this scale is adjusted so that the background has the same intensity as the diamond. The same lamps were used throughout the whole series of tests; they were mounted at about a height of 30 cm. above the table. There were screens, not shown in the diagram, to prevent direct light from the lamps reaching the eye of the observer. The red glass was a pure red of the kind used

for the signal lamps; it transmits from the red end of the spectrum to about 610  $\mu\mu$ , and is much purer than Wratten and Wainwright's standard tricolour red, which contains some yellow.

The tests were carried out between April 1922 and June 1923, partly in the Natural Philosophy Department of the University and partly in the Natural Philosophy Department of the Technical College. Altogether 604 students were examined, 56 women and 548 men. Of these 373 were University students, arts, pure science, engineers, and medicals, and 129 were day and 102 evening students at the Technical College. They made the test during the optical laboratory course, simply leaving the optical bench or whatever it was they were working at and returning to it when the test was completed. The distribution was essentially a random one: the observers were not selected in any way, but simply taken as they came, and no one who was asked to make the test declined.

In order to have conditions exactly the same in each case instructions were not given orally, but by means of a written card, which stated that "the light on the right-hand side was to be moved backwards and forwards along the metre stick until the white diamond and the surrounding red appeared of the same brightness." Each observer made three settings; the first of these was intended only to give familiarity with the apparatus and was consequently not recorded, but the second and third were recorded and their mean taken. The apparatus, it should be stated, worked very satisfactorily; it was simple and straightforward, and all the observers understood at once what was wanted.

Most observers, of course, find it extremely difficult to say when a white surface and a red one are equally bright. Helmholtz himself had no confidence in his judgment on this point. But it is easy to arrange that first the red, and next the white, is the darker of the two and then leave the lamp midway between these two positions, and this is how the observers usually proceeded.

As the scale was calibrated by an auxiliary experiment, it was possible from each observer's settings to state what fraction of the total light of the glow-lamp the red glass in question transmitted for him. The results varied from .086 for the man who was most red sensitive to .0015 for the man who was least red sensitive. This fraction specifies the observer's red sensitiveness. Its reciprocal specifies red blindness. Now in drawing the frequency curve the shape differs according as we use the fraction or its reciprocal as

abscissa. In the one case the left-hand side will be crowded together and the right-hand side extended, while in the other case the opposite will happen. If, however, we were to use the logarithm of the fraction or of its reciprocal as abscissa, the shape of the curve would be the same in each case. As there is no particular reason for preferring the ratio to its reciprocal, or *vice versâ*, we have stated the results in terms of the logarithm, and, in order to avoid negative characteristics, have chosen the logarithm of the reciprocal, or rather, for convenience in calculation, the logarithm of a number proportional to the reciprocal. The results are given in the following table, and are graphed in fig. 3, the women being shown in black. The  $\cdot 4$  in the first column of the table means  $\cdot 4$  and less than  $\cdot 5$ , the  $\cdot 5$  means  $\cdot 5$  and less than  $\cdot 6$ , etc.

Number specifying Red Blindness.	Men.	Women.	Total.
$\cdot 4$	1	0	1
$\cdot 5$	6	1	7
$\cdot 6$	25	5	30
$\cdot 7$	29	5	34
$\cdot 8$	57	10	67
$\cdot 9$	118	13	131
1.0	115	5	120
1.1	77	5	82
1.2	39	7	46
1.3	32	3	35
1.4	20	0	20
1.5	19	1	20
1.6	8	1	9
1.7	1	0	1
2.2	1	0	1
Total .....	548	56	604

The distribution is slightly asymmetrical, and there is one very red-blind observer very far out by himself, but we cannot definitely say, owing to the asymmetry, since there is only one, that he does not belong to the main group. In the red-green test and Rayleigh tests, described in previous papers\*, 13 men out of 835 and 29 men out of 423 respectively fell outside the continuous distribution. As the number of men in the present case is 548, the similar

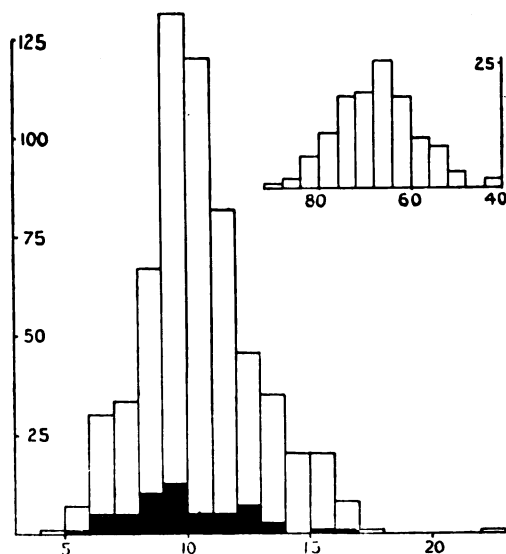
\* Houstoun and Dunlop, *Phil. Mag.* xli. p. 186 (1921); Houstoun, *Proc. Roy. Soc. A* cii. p. 353 (1922).

proportion would be 8.5 or 37.6. So it is clear that conditions are different here; so far as the present survey is concerned, normal variation covers everything.

Our results agree with those of Coblenz and Emerson as well as can be expected. Figs. 2 and 3 represent, of course, the variation of different quantities, but quantities that might certainly be expected to vary together.

Fig. 3.

Fig. 2.



In fig. 3 abscissæ represent insensibility to red light, ordinates number of observers. The decimal point has been omitted in the scale of abscissæ. In fig. 2 abscissæ represent sensibility to red light.

As the distribution was a random one, a number of the men, probably about 20, would be classed as colour blind. No systematic attempt was made to pick these out. But certain definite statements can be made about some of the observers.

First of all, the observer least sensitive to red, the man on the extreme right separated from the others by a large gap, has perfectly normal colour vision. He is an accurate and experienced observer, has made every one of the tests we have carried out in the past six years, and has never before shown any peculiarity; his performance in the

present test came as a surprise. His case is described fully as an example of normal colour vision in a recent paper\*, and yet the average man is about 18 times as sensitive to red light as he is. Edridge-Green† states that "a person with a considerable shortening of the red end of the spectrum will look at a red light (which is so dazzlingly bright to a normal sighted person as to make his eyes ache after looking at it closely for a few seconds) at a distance of a few inches, and remark that there is nothing visible, and that the whole is absolutely black." This is much more extreme than the case recorded above.

Again, the next ten observers, 1·6 and less than 1·8, on being questioned, stated that, as far as they themselves were aware, their colour vision was normal; also four observers who were known to be colour blind before making the test were placed respectively at ·87, ·55, ·62 and above 1·7. The fourth of these is not entered in the table and diagram, as he was a selected case, and did not belong to the random distribution that made the test.

There is no doubt whatever that certain individuals can be very insensitive to red and yet have excellent colour vision. It also seems true, from our own observations and the observations of others, that colour-blind individuals can, in certain cases, have normal sensibility in the red, but the probability is that they will also be abnormal in this respect.

We cannot assume that the distribution in fig. 3 is due to the superposition of a large symmetrical curve and a smaller one on its right due to the "red blind" of the original Young-Helmholtz theory, because most of the observers situated in this region have perfectly good colour vision.

Some of the "scatter" exhibited in the diagram is due to error of observation. A rough estimate of the influence of this cause was made in the following manner:—Two readings were, of course, recorded for each of the observers. The differences of these were taken, squared, added, and the root mean square extracted. The result was ·128. If we divide this by  $\sqrt{2}$  we obtain ·09 as the mean error of a single determination of the average observer. Hence, from an inspection of the diagram, probably one-quarter or one-fifth of the scatter of the main group was due to error of observation. The remainder is due to a real difference in the physiological equipment of the observer.

\* Proc. Roy. Soc. Edin. xlii. p. 75 (1922).

† 'The Physiology of Vision', p. 211.



§3. In a paper entitled "A Statistical Survey of the Colour Vision of 1000 Students," which has already been cited, Miss Dunlop and Dr. Houstoun give, on p. 191, the results of certain tests on the colour vision of 165 women students. Miss Dunlop tested another 148 women students after this paper was published, and it is now desired to substitute the following table for the second part of the table on p. 191:—

*Microscope Test. Results for 313 Women Students.*

Range.	Black.	Red-Green.	Blue-Green.	Range.	Black.	Red-Green.	Blue-Green.
1 & < 2	0	1	0	13 & < 14	58	41	38
2 & < 3	1	0	0	14 & < 15	30	36	48
3 & < 4	1	0	0	15 & < 16	15	43	50
4 & < 5	0	0	1	16 & < 17	9	36	33
5 & < 6	1	1	3	17 & < 18	2	34	24
6 & < 7	3	3	2	18 & < 19	2	24	20
7 & < 8	4	4	3	19 & < 20	0	11	24
8 & < 9	8	4	2	20 & < 21	0	6	11
9 & < 10	14	4	4	21 & < 22	0	5	1
10 & < 11	38	17	10	22 & < 23	1	1	3
11 & < 12	50	12	12	23 & < 24	1	1	3
12 & < 13	75	29	18	24 & < 25	0	0	3

When an observer makes the microscope test, owing to fatigue, inattention, differences in health, or other accidental variations he does not always obtain the same results. Some of the "scatter" exhibited in the diagrams of the former paper is due to this cause, and not to difference in the physiological equipment of the observers. In the former paper no indication is given of how much of the scatter is due to this cause, but as each observer made two readings, it is possible in the manner described above to show that, in the case of the red-green test, when the 13 observers in the "tail" are omitted, about four-tenths of the scatter is due to error of observation, both in the case of the men and the women. The women do not give more consistent results than the men; also the observers on both sides of the main curve are equally erratic.

July 1923.

LXXIX. *The Effect of the Rolling of a Ship on the Readings of a Marine Mercury Barometer.* By M. A. GIBLETT, M.Sc., Assistant Superintendent, Forecast Division, Meteorological Office, Air Ministry\*.

1. **T**HIS paper is devoted to an investigation of the effect on the readings of a marine mercury barometer of a periodic motion of the point of support, such as would be associated with the rolling (or pitching) of a ship. It arose from some comparative readings of a marine Kew pattern mercury barometer and an Admiralty Mark I. aneroid barometer, made on a trawler on the North Sea, from which it is deduced below that at times the mercury in the former was depressed below its true level, remaining so, without "pumping," for considerable periods. It is not found possible to explain this behaviour on the basis of the results of previous investigations into the errors to which a mercury barometer is subject at sea, which are summarized in paragraph 2. These do not seem to have included the effect of the forced oscillations of the instrument due to rolling, which is here shown to be of the kind observed.

2. In a paper contributed to the 'Quarterly Journal of the Royal Meteorological Society' in 1908, Gold showed that the effect of a vertical simple harmonic motion of the point of support of the instrument, such as would arise from the heaving of the ship, is an oscillation of the mercury about its *true* height as mean, with an amplitude depending on the constriction of the tube. The greater the "lagging time" of the instrument the smaller the amplitude, which, however, may still be appreciable for instruments with the normal lagging time of 4 minutes. In a case investigated, the range of the oscillation was of the order of two-thirds of a millibar, "pumping" thus being still sufficiently great to introduce uncertainties into the readings. Another source of error investigated was the free oscillation of the barometer about its point of support, the effect of which is to cause the mercury to oscillate about a mean level differing from the true height of the column. Whether the mean displacement of the mercury is one of depression or elevation depends on whether the centrifugal force on the mercury, due to the swing, is sufficient to overcome the tendency of the mercury to run up the tube when the latter is inclined to the vertical, and this depends on the construction of the barometer. For

\* Communicated by the Director, The Meteorological Office, Air Ministry.

Kew pattern barometers of the kind commonly in use the result is an *elevation* of the mercury above its true height by a mean amount which may, for small oscillations of the instrument, be of the order of a millibar. (The amplitude of the oscillation about this new mean height is in this case rendered negligible by the constricted tube.) Duffield and Littlewood \* have since shown how an adjustment may be made to a Kew pattern marine barometer so that the two opposing influences above may be made to neutralize one another for small amplitudes of swing, thus eliminating this source of error.

Now, in the paper already cited, Gold made a comparison of barometer readings taken on ships crossing a line between Falmouth and Brest with values deduced from readings at these two places, with the result that in practically all cases the ships' observations were markedly *lower* than would be expected from the shore readings, by an amount varying between wide limits. A partial explanation of this was found in the further source of error arising at sea from greater exposure to wind, which may exert a considerable suction effect if, say, the barometer is located in the chart-room with the lee-door open. But, even allowing for this, there remained on an average a further depression of the mercury of the order of two-thirds of a millibar to be accounted for, and it was suggested that the practice of reading the lowest instead of the average height of the mercury when "pumping" would contribute to this. The present results show that the effect of rolling would also contribute.

3. The observations were taken incidentally during an official cruise on the North Sea on the 'George Bligh,' a steam trawler of the 'Mersey' type, belonging to the Ministry of Agriculture and Fisheries. The mercury barometer was set up in a deck-house approximately amidships, and was placed centrally as regards distance from the ship's sides. Its cistern was about 8 feet above water level under calm conditions. The aneroid was placed close to the mercury barometer, at cistern level, and only set roughly. It was very unfortunate that circumstances did not permit of a set of comparative readings being taken immediately before leaving port and again immediately after arrival back, but a comparison was made on land in November of the same year. The pairs of readings at sea in August numbered 61, spread irregularly over 8 days, and the differences ranged over 2.6 mb. about the mean difference

\* Phil. Mag. xlii. pp. 166-173, July 1921.

0.47 mb.\* The pairs of readings on land in November numbered 43, spread irregularly over a period of more than a month, during which pressure varied through the same part of the scale as at sea in August. The difference on land ranged over 0.8 mb. only, about a mean of 1.1 mb., the standard deviation being 0.21 mb. If we could assume that the result of this comparison would have been the same had it been made in August immediately on reaching port, then we could infer that at sea there was a considerable number of differences outside this range on the negative side, such as could only be explained by some factor, operative at sea only, depressing the mercury in the one barometer without affecting the aneroid, or causing the latter to read too high without affecting the mercury barometer. This is clear from the following table showing the frequency distribution of the differences at sea :—

TABLE I.

(Showing frequency distribution of differences between readings of mercury and aneroid barometer at sea \*.)

Difference (mb.)	-1.0 to -0.8	-0.7 to -0.5	-0.4 to -0.2	-0.1 to 0.1	0.2 to 0.4	0.5 to 0.7	0.8 to 1.0	1.1 to 1.3	1.4 to 1.6
Frequency	2	1	4	4	12	22	9	5	2

(Mean difference 0.47 mb.; range 2.6 mb.)

There is no reason to suppose that the range of 0.8 mb. and the standard deviation of 0.21 mb. would have been appreciably different on land in August, but the mean difference 1.1 mb. might have been, as I cannot be certain that the adjustment of the aneroid was the same. However, two readings taken while at anchor in Bridlington Bay in calm weather can be regarded as having been made under similar conditions to those on land, and the ship was remarkably steady on one occasion at sea. The differences in these cases were 0.7, 0.9, and 0.8 mb. Now the probable error of a mean value from  $n$  observations is  $\frac{2}{3} \frac{\sigma}{\sqrt{n}}$ . Here  $n=3$

\* A positive difference indicates reading of mercury barometer higher than aneroid.

and  $\sigma = 0.21$  from the November comparison (based on 43 observations), so that the probable error in accepting 0.8 mb. as the mean about which the differences would have been distributed in a series of observations on land with the August setting of the aneroid is less than 0.1 mb.

Thus the above conclusion is still justified. Now the two factors operating at sea and not on land are the additional exposure to wind and the motion of the ship. Any sustained suction or pressure effect of the wind on the pressure in the deck-house should affect both instruments equally. It is also difficult to see how the motion of the ship could cause the aneroid barometer to read too high, so that it appears probable that the motion of the ship was at times such as to cause a persistent depression of the mercury in the mercury barometer of the order of 1 mb., persistent, because similar differences between the readings of the two instruments occurred in spells, and, further, there was no appreciable "pumping" of the mercury at any time during the cruise. From § 2 it follows that if this was the case it must have arisen from the rolling of the ship, and it remains to investigate the possibility of this.

4. The following notation is employed:—

$d$ , the distance of the point of support of the barometer from the axis about which the ship rolls.

$\phi$ , the angle of inclination of the ship to the vertical at any instant.

$x$ , the corresponding displacement of the point of support of the barometer. ( $x = \phi d$ .)

$\phi_m$ , the maximum value of  $\phi$ .

$b$ , the maximum value of  $x$ . ( $b = \phi_m d$ .)

$T$ , the period of the roll. ( $T = 2\pi/n$ .)

$L$ , the length of the corresponding simple equivalent pendulum.

$\theta$ , the angle of inclination of the barometer to the vertical at any instant.

$\lambda$ , the maximum value of  $\theta$ .

$\tau$ , the period of the barometer for free oscillations about its point of support. ( $\tau = 2\pi/m$ .)

$l$ , the length of the corresponding simple equivalent pendulum.

$\zeta$ , the distance of the centre of the mercury column from the point of support of the instrument.

$R, r, \rho$ , ratios defined by  $R=L/l=T^2/\tau^2$ ,  $r=b/l$ ,  $\rho=\xi/l$ .

$h$ , the true height of the barometer.

$z$ , the actual length of the mercury column at any instant.

$h'$ , the mean length of the mercury column while oscillating.

$\delta$ , the corresponding relative error in the readings.

$\delta=(h-h')/h$ .

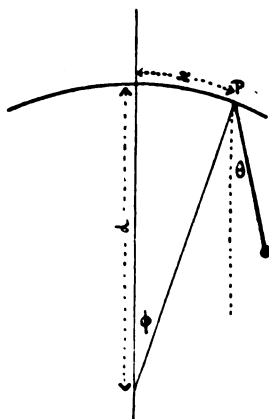
$\beta$ , the amplitude of the oscillations of the mercury column.

$1/q$ , the "lagging time" of the barometer.

$h''$ , a length greater than  $h$ , depending on the constriction of the barometer tube.

5. Let us then examine the effect of a periodic displacement of the point of support  $P$  of a marine mercury barometer given by  $x=\phi d=b \cos nt$ , where  $d$  is the distance of  $P$  from the axis about which the ship rolls,  $\phi$  is the angle of inclination of the ship at any instant to its equilibrium position,

Fig. 1.



and  $x$  is the length of the corresponding circular arc described by  $P$  (fig. 1). If  $\theta$  be the inclination of the instrument at any instant to the vertical, the equation of its motion is

$$l\ddot{\theta} + g \sin \theta + \ddot{x} \cos (\theta + \phi) - \frac{\dot{x}^2}{d} \sin (\theta + \phi) = 0,$$

where  $l$  is the length of the simple equivalent pendulum for

free oscillations of the barometer about its point of support. If  $\theta$  and  $\phi$  are small this may be written approximately

$$l\ddot{\theta} + g(1 - \dot{x}^2/gd)\theta + \ddot{x}(1 - \dot{x}^2/d\dot{x}) = 0$$

$$\text{or } l\ddot{\theta} + g\{1 - \phi_m^2(\sin^2 nt)4\pi^2 d/T^2 g\}\theta + \ddot{x}(1 + \phi_m^2 \sin^2 nt) = 0,$$

where  $\phi_m = b/d = \text{angle through which ship rolls on either side of the vertical}$ , and  $T$  is the period of the roll.

Now

$$4\pi^2 d/T^2 g = 1.23d/T^2$$

(units foot, second), and in practice it would scarcely be necessary to consider cases in which  $d/T^2 > 1$ , so that,  $\phi_m$  being assumed small, the equation of motion may further be written approximately

$$l\ddot{\theta} + g\theta + \ddot{x} = 0.$$

Writing  $m^2 = g/l$ ,  $n^2 = g/L$ ,  $r = b/l$ ,  $R = L/l$ , and  $\lambda = r/(R-1)$ , the solution of this equation may be shown to be

$$\theta = \lambda \cos nt + A \cos (mt + \epsilon),$$

where  $A$  and  $\epsilon$  are arbitrary constants. The term  $A \cos (mt + \epsilon)$  merely represents a free oscillation of the instrument, of arbitrary amplitude and phase, superimposed on the forced oscillation given by  $\lambda \cos nt$ . The effect of the free oscillation alone has already been referred to in § 2, and it is our present purpose to consider the forced oscillation given by

$$\theta = \lambda \cos nt,$$

supposing the free oscillation absent.

Now the column of mercury may be regarded as subject to an acceleration along the tube, relative to the instrument, equal to

$$g \cos \theta + \zeta \theta^2 - \ddot{x} \sin (\theta + \phi) - \frac{\dot{x}^2}{d} \cos (\theta + \phi),$$

where  $\zeta$  is the distance of the centre of the column from the point of support. Supposing  $\theta$  and  $\phi$  small, this may be expressed as a function of  $t$  in the form

$$g \left[ 1 + \frac{r^2(R+2\rho-2)}{4R(R-1)^2} + \left\{ \frac{r^2(R-2\rho-2)}{4R(R-1)^2} + \phi_m^2 \cdot \frac{4\pi^2 d}{T^2 g} \right\} \cos 2nt \right], \dots \quad (A)$$

where  $\rho = \zeta/l$ .

Calling the constant part  $g + g'$ , suppose that under the action of this the mercury assumes a height  $h'$  instead of

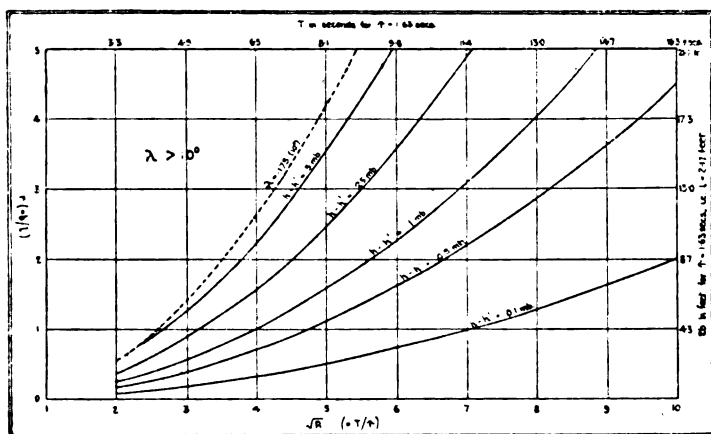
the true height  $h$ . Then  $hg = h'(g + g')$ , so that,  $g'$  being small compared with  $g$ ,

$$\delta = (h - h')/h = g'/g = \frac{r^2(R + 2\rho - 2)}{4R(R - 1)^2} \quad (B)$$

It is evident that the periodic acceleration represented by the third term of (A) above would cause oscillations of the mercury about the mean height  $h'$ , and, if the amplitude of these were rendered negligible by the constriction of the tube, then the mercury would simply assume a steady height  $h'$  instead of  $h$ .

6. The relative error,  $\delta$ , due to the forced oscillation, is given by (B) in terms of the three ratios  $\rho (= \zeta/l)$ ,  $r (= b/l)$ , and  $R (= L/l = T^2/\tau^2)$ , where  $\zeta$  is the distance of the centre

Fig. 2.



Showing the amount of depression of the mercury in a marine mercury barometer, due to the rolling of a ship. (For explanation see § 6.)

of the mercury column from the point of support,  $l$  is the length of the simple equivalent pendulum for free oscillations of the barometer about its point of support (period  $\tau$ ),  $b$  is half the arc along which the point of support moves, and  $L$  is the length of the simple equivalent pendulum for the forced oscillations (period  $T$ ). We may here also usefully recall that the amplitude of the forced oscillation of the barometer is given by  $\lambda = r/(R - 1)$ , and that the expression for  $\delta$  given by (B) has been obtained on the supposition that



$\lambda$  is small. In fig. 2 abscissæ represent values of  $\sqrt{R}$ , and ordinates values of  $r$ . Pairs of values corresponding to points on the dotted line are such as to make  $\lambda=10^\circ$ . Attention will be confined to pairs of values of  $R$  and  $r$  corresponding to points lying to the right of the dotted line, for which  $\lambda < 10^\circ$ .

From (B) it is seen that  $\delta$  is positive, *i. e.*, the forced oscillation causes a *depression* of the mercury, if  $R > 2(1-\rho)$ . For the barometer employed on the trawler, which may be taken as typical,  $\tau=1.63$  secs., so that  $l=2.17$  ft.  $\zeta$ , by direct measurement, was about 5 ins. for a barometric height of 30 ins., and thus  $\rho$  was a fraction like  $1/5$ , varying somewhat with the height of the barometer. Hence  $\delta > 0$ , if  $R (=T^2/\tau^2) > 1.6$ , *i. e.*,  $T > 1.3\tau$ , which would in general be the case at sea. It may here be noted that the adjustment suggested by Duffield and Littlewood (see § 2) is such as to make  $\rho=1/2$ , in which case the condition for  $\delta > 0$  would be  $R > 1$  or  $T > \tau$ .

The depression of the mercury corresponding to different values of  $R$  and  $r$ , for  $\rho=1/5$ , and  $h=1000$  mb.\*, is indicated in fig. 2 by means of curves along any one of which it is constant.

The curves may also be read in conjunction with the scales for  $T$  and  $2b$ , at the top and on the right of the diagram, in the particular case when  $\tau=1.63$  seconds (and  $\therefore l=2.17$  feet).

7. The amplitude of the forced oscillations of the mercury may be investigated by adapting to the present case the equation of motion of the mercury as given by Gold † for the case of free oscillations of the barometer. It may then be written

$$h''\ddot{z} + \frac{g}{q}\dot{z} + \left\{ g \cos \theta - \ddot{x} \sin (\theta + \phi) - \frac{\ddot{x}^2}{d} \cos (\theta + \phi) + \zeta \dot{\theta}^2 \right\} z - gh = 0,$$

where  $h''$  is a length ( $> h$ ) depending on the constriction of the tube,  $z$  is the actual length of the mercury column at any instant, and  $1/q$  is the "lagging time" of the barometer.

\* The values of the depression would be appreciably the same for other pressures, being changed proportionately.

† *Loc. cit.* § 2.

If  $\theta$  and  $\phi$  are small this equation may be written approximately

$$h''z + \frac{g}{q}z + g\{z - h(1 - \delta)\} + gh\delta' \cos 2nt = 0,$$

where

$$\delta = \frac{r^2(R + 2\rho - 2)}{4R(R - 1)^2} \quad \text{and} \quad \delta' = \frac{r^2(R - 2\rho - 2)}{4R(R - 1)^2} + \phi_m^2 \cdot \frac{4\pi^2 d}{T^2 q},$$

both being small fractions under the conditions assumed.

The required solution of this is

$$z = h(1 - \delta) + \beta \sin(2nt + \psi),$$

where

$$\beta = gh\delta' / \{q^2(1 - 16\pi^2 h''/gT^2)^2 + 16\pi^2/T^2\}^{\frac{1}{2}}. \quad (C)$$

Thus the mercury oscillates about a mean height  $h'$  given by

$$h' = h(1 - \delta).$$

This gives  $\delta = (h - h')/h$ , as obtained otherwise in § 5.

8. To evaluate the amplitude ( $\beta$ ) of the oscillations of the mercury let us take, following Gold,  $h'' = 5$  ft. and  $q = 1/240$ . Further take  $l = 2.2$  ft. Then in the denominator of (6) the first term may be neglected in comparison with the second, so that approximately

$$\beta = qh\delta'T/4\pi.$$

Now, from § 7,

$$\delta' = Q + \phi_m^2 \cdot 4\pi^2 d/gT^2,$$

where  $Q < \delta$ , whence

$$\beta = hQ \cdot qT/4\pi + h\pi dq\phi_m^2/gT.$$

But  $hQ < h\delta$ , which is the quantity represented in fig. 2, so that evidently the first term may be neglected, being, for values of  $T$  considered, only a very small fraction of a millibar. Hence approximately

$$\beta = h\pi dq\phi_m^2/gT. \quad (D)$$

If we suppose  $\phi_m < 0.175$  radian (*i.e.*  $10^\circ$ ), and  $d < 50$  feet, then  $\beta < h/1600 T$ , so that if  $T > 5$  secs., say,  $2\beta$  is less than 0.25 mb., and in general considerably less.

9. The effect of the forced oscillations of the instrument on its readings has been examined above only for small angles of roll of the ship, but it is found that even such may result in a persistent depression of the mercury by an amount which is not negligible. Pumping is, however, not likely to

be marked in such cases. The effect is thus precisely that observed on the North Sea, and the magnitude too is quite in agreement. The conditions encountered on the North Sea were such as to produce a forced oscillation of period 6 to 7 seconds. As a very rough estimate we may take the point of support of the barometer as having been 10 ft. above the axis about which the vessel was rolling. A roll of only  $10^\circ$  each side of the vertical would then imply that the point of support ranged through 3.5 ft. From fig. 2 we see that  $T=6.5$  secs. and  $2b=3.5$  ft. correspond with a depression of the mercury between 0.5 and 1 mb., which is of the requisite magnitude. Further (D) in § 8 shows that pumping in this case would be negligible.

The period of the forced oscillation in the particular case discussed is small. For longer periods fig. 2 shows that the depression of the mercury is negligibly small unless the point of support of the barometer ranges through a considerable distance. However, the usual practice of placing the barometer for convenience in the chart room favours this, resulting as it does in the instrument being well above the axis about which the ship rolls. For example, the barometer is commonly 30 or 40 feet above the water-plane, and the ship may be considered roughly as rolling about an axis lying between the water-plane and half-draught \*. A roll of only  $10^\circ$  on either side of the vertical might accordingly result in the point of support of the barometer ranging through about 14 feet ( $2b=14$ ), and fig. 2 shows that, corresponding to this, the barometer would read 1 mb. too low if the period were between 11 and 12 seconds, and 0.5 mb. if the period were nearly 14 seconds. It is evident that, while in many cases the effect might be negligible, yet for accurate work it would always be advisable to mount the instrument as near as possible to the axis about which the ship rolls. An interesting case of the different behaviour of two barometers placed in different parts of a ship was mentioned in the discussion of Col. Gold's paper † by Capt. R. C. Warden. Under ordinary weather conditions the instruments agreed, but during the passage of two typhoons in the China Seas their readings differed. It is possible that this was due to the different effects of the forced oscillations of the instruments during the disturbed period, owing to their different locations in the ship.

\* 'Admiralty Manual of Seamanship,' 1909, vol. ii. p. 571.

† *Loc. cit.* § 2.

LXXX. *Notices respecting New Books.*

*Tables of the Incomplete  $\Gamma$  Function.* Edited by KARL PEARSON, F.R.S. £2 2s. (His Majesty's Stationery Office, Kingsway, W.C. 2.)

SEVERAL important sets of tables have been calculated by the Staff of the Department of Applied Statistics in connexion with the Gamma and similar functions. The difficult and laborious computation of the Incomplete  $\Gamma$  function has also been undertaken by members of this Staff, who have placed those interested in applied mathematics under a great obligation through the completion of these valuable tables. The fact that this volume contains some fifty thousand seven-figure values with second and fourth differences for the two variables, will give some idea of the magnitude of this arduous undertaking, "a painful work" indeed.

In order to overcome the difficulty arising from the large range of values of the function, the ratio of the Incomplete to the Complete  $\Gamma$  functions is tabulated, restricting the entries between

the limits zero and unity: the variable  $x$  in  $\int_0^x e^{-t} t^p . dt$  is replaced by a variable  $u$  connected with  $x$  by the relation  $u = x / \sqrt{p+1}$ .

The introduction sets out fully the methods of using the tables and computing intermediate values of the function by the various interpolation formulae. Although thousands of entries are given in this volume, these interpolations may be considerable, but in comparison with the labour required in building up the tables, the computer's work is well-nigh insignificant.

It is encouraging to note that, on the recommendation of the Advisory Council, the Department of Scientific and Industrial Research have undertaken the publication of this work: the publication of tables of other functions related to the Gamma function also deserves the real assistance which has been accorded to this volume.

*Mathematical Tables.* By G. H. BRYAN, Sc.D., F.R.S.  
(Macmillan & Co.) 3s. 6d.

IN addition to the tables of the six trigonometric functions and their logarithms, which form the greater part of this book, Prof. Bryan has included the Bordered Antilogarithm Table, giving logarithms, antilogarithms, and logarithms of reciprocals. The entries in this short and compact table are to five places for smaller values of the logarithm, with proportional differences of one or two digits. The table of squares can be employed to better effect for the calculation of square roots than by the use of logarithms. In the methods of using the tables, special attention is given to the Antilogarithm Table, the most important feature of this collection.

LXXXI. *Proceedings of Learned Societies.*

GEOLOGICAL SOCIETY.

[Continued from p. 576.]

April 18th, 1923.—Prof. A. C. Seward, Sc.D., F.R.S., President, and, afterwards, Dr. Herbert H. Thomas, M.A., Vice-President, in the Chair.

**T**HE following communication was read :—

‘The Structure of the Bowmore-Portaskaig District of Islay.’

By John Frederick Norman Green, B.A., F.G.S.

The island occupies a critical position in connexion with present controversies in Highland geology, because (a) rocks of the Eastern Highland type there approach the North-West Highland rocks; (b) in it cross the lines of work of researchers of different schools; and (c) over much of the island the original characters of the rocks are exceptionally preserved.

All observers agree that the western peninsula (the Rhinns) is composed of Lewisian gneiss overlain by Torridonian. The author deals only with the northern and central parts of the main island.

In this part the Geological Survey, in a memoir published in 1907, regarded a dolomitic group as probably Cambrian, preserved in synclines of older quartzite, at the base of which a conglomerate (Portaskaig Conglomerate) with granite (nordmarkite) and other boulders, rested upon limestone (Islay Limestone) and dark slates (Mull of Oa Phyllites): the whole series being brought by a great thrust (Loch Skerrols Thrust) over Torridonian (Bowmore Sandstone).

Later, Mr. E. B. Bailey, in a paper read in 1916, held that the dolomitic group was intercalated between a ‘Lower Quartzite’ connected with the Conglomerate and an ‘Upper Quartzite’ (the Islay Quartzite), confirming otherwise on the whole the Survey views, and correlating the Loch Skerrols Thrust with the Moine Thrust; but Mr. Barrow (in discussion) considered that the thrust had no existence, that the Bowmore Sandstone was not separable from the rocks east of the supposed thrust, and that the sequence should be inverted, the limestone overlying the conglomerate, which in turn overlay the dolomitic group and the Islay Quartzite.

The author’s attempt to find the correct interpretation has necessitated a quantitative definition of the term ‘quartzite,’ which has previously been used to cover a wide range of rocks in Islay. For the purpose of this paper a limit of 10 per cent. of felspar has been adopted, more highly felspathic rocks being termed ‘arkose.’ On this definition the Islay ‘Upper’ Quartzite is throughout true quartzite; but the so-called ‘Lower Quartzite’

is not quartzitic, being composed of arkoses and greywacke-slates identical with the matrix of the Portaskaig Conglomerate. As much of the latter horizon is not conglomeratic, and no dividing line can be drawn between the two, they have been grouped together as the Portaskaig Beds. Thus the dolomitic group intervenes between the Portaskaig Beds and the Islay Quartzite.

It is next shown that the supposedly Torridonian Bowmore Sandstone consists of arkoses and flags, the former being identical in all respects with the matrix of the Portaskaig Beds, and containing in places similar pebbles, including the characteristic nordmarkite. The flags, which, owing to isoclinal folding, have apparently an enormous thickness, are identical in minute detail with certain siliceo-argillaceous flags that always occur in the dolomitic group next to the Islay Quartzite. They are termed the Bowmore Flags.

Thus there is no change of facies at the supposed thrust, and an examination of its presumed line of outcrop proves that the rocks are folded up without disruption, except for some shearing on the reversed limbs of overfolds. The Loch Skerrols Thrust is non-existent.

The relations of the dolomitic group are then investigated, and it is found, first, that the Bowmore Flags are perfectly conformable to the white edge (a well-marked horizon) of the Islay Quartzite; but secondly that they, and the dolomitic flags associated with them, are partly or wholly cut out in places by the Portaskaig Beds. It is inferred that the latter are younger than the dolomitic group, from which they derive material.

The sequence within the dolomitic group appears to be reversed along Islay Sound. It is shown, however, that this misleading section can be explained by a combination of erosion and isoclinal folding.

These conclusions necessitate a re-examination of the evidence at Beannan Dubh, which has been taken to prove that the Portaskaig Beds are younger than the Limestone, and therefore older than the dolomitic group. Reasons are adduced for regarding the supposed disposition of strata in this neighbourhood in nearly horizontal beds as deceptive, the rocks actually lying in isoclinal folds with low dip, by which the Portaskaig Conglomerate is brought up in anticlines. On Beannan Dubh a dolomite-breccia resting upon a thin band of dolomite within the Portaskaig Beds, which has been believed to prove superposition, is regarded by the author as a desiccation-breccia and shown to be repeated in a reversed position. The evidence of solution-hollows is considered to favour true superposition of the dolomite-band on the breccia, supporting the view that the Limestone is younger than the Portaskaig Beds.

Thus all lines of evidence converge to prove the order of succession proposed by Mr. Barrow, and the structure of Islay is synclinal, not anticlinal. Only one system of folding is required to explain the facts.

LXXXII. *Intelligence and Miscellaneous Articles.*

## ON IONIC OSCILLATIONS IN THE STRIATED GLOW DISCHARGE.

*To the Editors of the Philosophical Magazine.*

GENTLEMEN,—

**I**N the May number of the *Philosophical Magazine* appears a paper by Dr. Appleton and Mr. West dealing with the discontinuous nature of the vacuum-tube discharge under some conditions and the consequent radiation therefrom.

I am venturing to point out, with your permission, that the literature of the subject is not without references to this phenomenon, which, indeed, to those who have worked with discharge-tubes running under steady voltage conditions, must be familiar.

As just two early examples may I cite

I. *M. Cantor*, Wied. Annal. 67, ii. (1899).

This investigator performed an experiment strikingly similar to that of Messrs. Appleton and West. He showed quite conclusively that electric waves were radiated from a discharge-tube under certain conditions of steady voltage supply, and specifically mentions a number of precautions designed to eliminate all possibility of the mere starting of the discharge producing the radiation.

II. *Rieche*, Ann. d. Phys. iv. (1901).

This investigator looked into the matter from the point of view of the variation of the current and luminosity in the tube, by the use of a telephone and a rotating-mirror respectively. By this time, the phenomenon of periodic intermittence of the discharge (tube run from a battery of accumulators under certain conditions) appears to be a commonplace, for he remarks:—"bei höheren Drucken das bekannte Flackern des Glimmlichtes eintret. Ihre Anzahl in der Sekunde schwenkte von 50 bis über 2000."

The frequency was determined in a most ingenious way by observing simultaneously in the rotating mirror the reflexion of the discharge-tube and that of a sensitive flame jumping with a known and variable frequency.

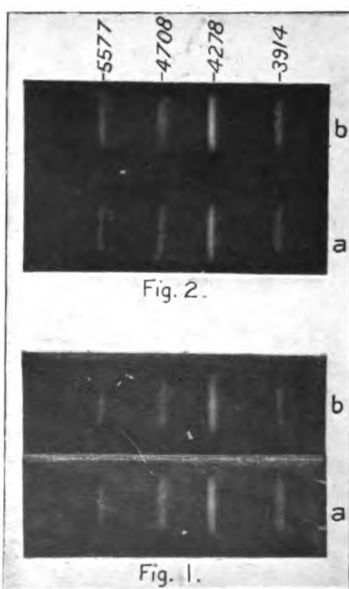
Yours faithfully,

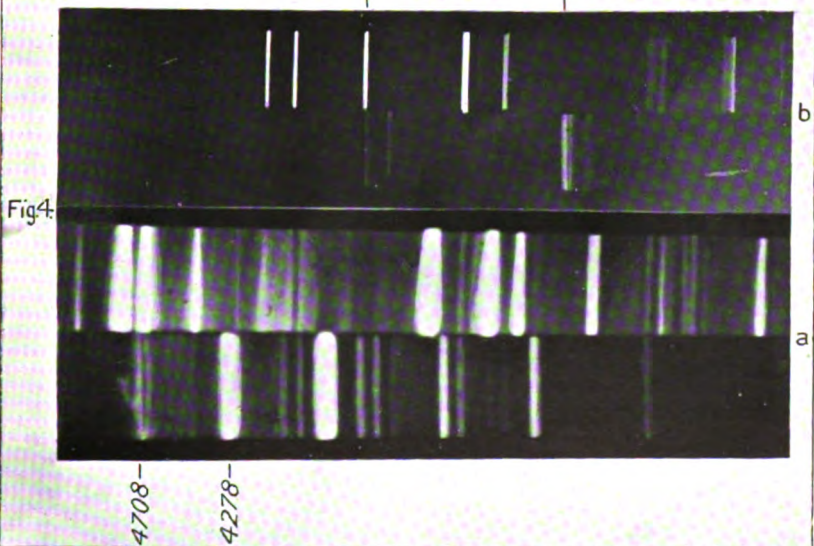
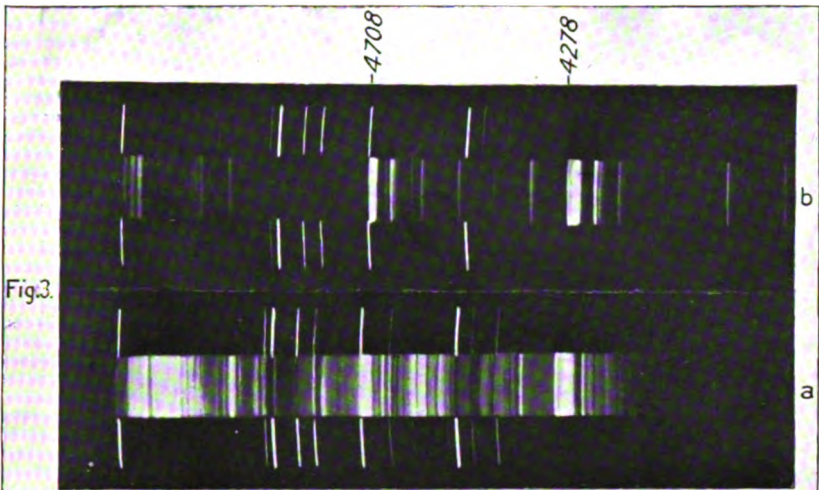
R. WHIDDINGTON.

The Physics Laboratories.  
The University, Leeds.  
25th June, 1923.











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[SIXTH SERIES.]

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NOVEMBER 1923.

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LXXXIII. *The Excitation of Characteristic X-rays from certain Metals.* By FRANK HORTON, *Sc.D., F.R.S.*,  
URSULA ANDREWES, *M.Sc.*, and ANN CATHERINE DAVIES,  
*D.Sc.*\*

THE well-known researches of Moseley established the fact that the characteristic X-ray spectra of the elements change in an orderly manner as we pass from element to element down the Periodic Table. This regularity has received theoretical explanation on the basis of Bohr's theory of atomic structure, according to which the X-ray spectra arise from the removal of an electron from one of the inner electronic groups of the atom and the subsequent readjustment of the remaining electrons of the system. Thus the K series of characteristic emission lines arises from the displacement of an electron from the innermost group, which, according to the theory, is complete in the helium atom and remains unaltered throughout the elements of higher atomic number. The binding of the two electrons in this group in any atom depends on the nuclear charge, but is practically independent of the presence of electrons in the groups of higher quantum number.

In the process of atom building the L, M, etc., electronic groups do not attain completion until elements of higher atomic numbers are reached (*e. g.*, the L group until neon for which  $z=10$ ); but after each group is completed in turn, the binding to the nucleus of the electrons in this group is

\* Communicated by the Authors.

*Phil. Mag.* S. 6. Vol. 46. No. 273. Nov. 1923.

3 A

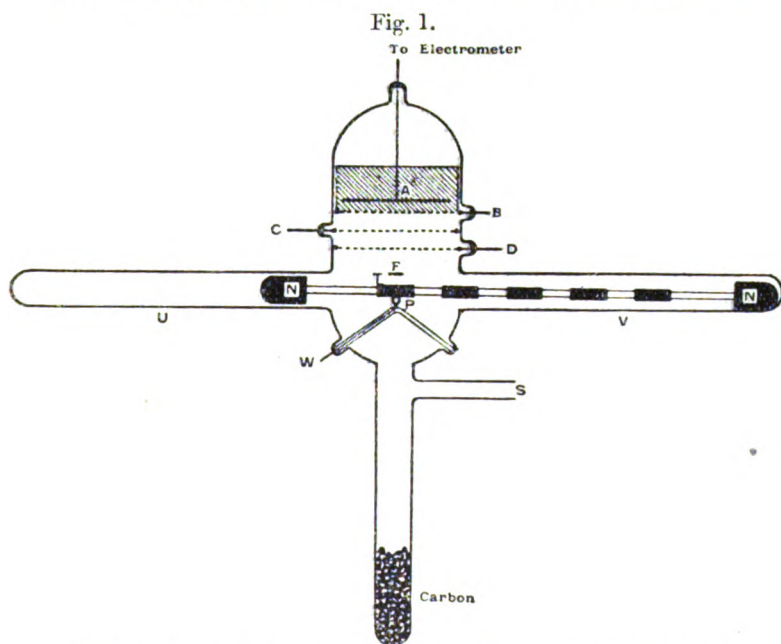
influenced mainly by the increasing charge on the nucleus, as we pass from element to element, and only to a secondary extent by the electrons which gradually fill up the outer groups. The existence of the Moseley relation between the atomic numbers of the elements and the frequency of any particular X-ray emission line (or absorption limit) of those elements, is attributed to this persistence of the inner groups unchanged throughout the elements of atomic numbers higher than those at which each group is complete. In accordance with theory, it would be expected that in passing down the Periodic Table the Moseley relation for any given set of lines (or absorption limits) would cease to hold at the element at which a change occurs in the constitution of the particular electronic group to which the set of lines is due. On Bohr's view of the process of the binding of the electrons to the nucleus, the M group changes between the elements calcium ( $z=20$ ) and copper ( $z=29$ ) from a system containing two sub-groups of four electrons each to a system containing three sub-groups of six electrons each. The energy required to remove an electron from any one of these sub-groups corresponds to one of the M X-ray absorption limits. Experimental evidence suggests that the third M sub-group of electrons commences at scandium ( $z=21$ ), and that the development of the M shell to three sub-groups of six electrons each is for the first time complete at copper ( $z=29$ ), but so far as the authors are aware, no details have been published of the constitution of the M group in the elements of atomic numbers between 22 and 29. It seemed possible that evidence bearing on this point might be obtained from observations of the excitation potentials required to produce the characteristic M radiations of the elements with atomic numbers in and near this region.

The excitation potential method of investigating X-ray absorption limits consists in measuring the photoelectric current caused by the X-radiation emitted by a given element under electronic bombardment with gradually increasing energy of the electron stream, and in determining, from the positions of discontinuities in the current-potential curves, the critical points at which new radiations are produced. This method of experimenting is particularly valuable for investigations in that part of the spectrum between the longest wave-length measurable with an X-ray spectrometer and the shortest wave-length measurable with a vacuum grating spectroscopic, an interval which is at present about three octaves.

The present paper records the results of observations by this method on the elements iron, nickel, copper, and zinc, which fall within the region of atomic numbers referred to. The excitation potentials for aluminium have also been investigated, and the results are included. Investigations by this method, of the potentials of excitation of characteristic X-radiations from some of these elements, have recently been published by Kurth\* and by Mohler and Foote†, and their results will be referred to in the course of the paper.

*Apparatus and Method.*

It is essential for the success of the experiments that the electronic bombardment of the element under test should be



carried out in a vacuum as nearly perfect as it is possible to obtain. The glass vessel in which the electrodes were contained was therefore constructed without any waxed or cemented joins. It had a tube (see fig. 1) 2 cm. wide, containing charcoal which was cooled in liquid air during the observations, and it was connected by a side tube S, through

\* E. H. Kurth, *Phys. Rev.* xviii. p. 461 (1921).

† F. L. Mohler and P. D. Foote, *Sci. Papers, Bur. of Standards*, No. 425.



a wide bore stop-cock and a U-tube immersed in liquid air, with a diffusion pump which was maintained in operation throughout the measurements. Before beginning the observations, the apparatus was pumped out and the residual gas removed as completely as possible from the filaments, electrodes, and glass walls of the apparatus by long-continued heating in an air oven and simultaneous pumping with the diffusion pump.

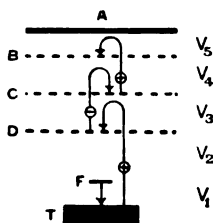
The metals which formed the targets for the electron bombardment were supplied as pure by Messrs. Johnson, Matthey & Co. They were arranged in a row on two parallel thin quartz rods which ran through holes drilled in them. Each target was 2 cm.  $\times$  1 cm.  $\times$  0.5 cm., and they were kept apart by pieces of quartz tubing 1.5 cm. long which fitted over the rods in the spaces between the metals. The extreme ends of the quartz rods fitted into two pieces of soft iron as indicated in the figure (N, N), so that by means of electromagnets the whole row could be moved along the horizontal tube U, V, and each target in turn could be placed underneath the tungsten filaments F which supplied the bombarding electron stream. An electrical connexion to the particular element under examination was made by means of the platinum wire W, at the upper end of which was a small platinum ball P, which pressed against the lower face of the target. This arrangement has the great advantage that the element under investigation can be quickly changed so that each element can be examined in turn, and it can be rapidly ascertained whether an indication of a critical point in a current-voltage curve is a genuine effect due to the element, or whether it arises from some other cause, in which case it would be common to the whole series of curves. The row of targets could be turned over in the apparatus by means of an electromagnet so that the arrangement permitted of the use, in turn, of both faces and both edges of each target. Thus a considerable surface of each was available for bombardment, and the part in use could be changed as soon as it showed signs of being contaminated by the sputtering of the glowing filaments. In the actual apparatus, the tubes U and V were rather longer than they are represented as being in the figure. This allowed of the whole row of targets being moved into one or other of these tubes during the preliminary heating of the filaments in the process of ridding them of occluded gases, so that the surface of the targets was not contaminated during this process.

The apparatus contained two V-shaped tungsten filaments,

each about 1.5 cm. long in the glowing portion. They were introduced from opposite sides of the main glass tube, and were close together in the same horizontal plane in the position indicated by F in the figure. In most of the earlier observations only one filament was used at a time, the other being kept in reserve; but in many of the later experiments the two were used simultaneously, for it was found that the increased bombardment thus obtained made the effects sought for more marked.

The radiations stimulated by the electron bombardment of the targets were detected by means of their photoelectric effects on a platinum plate A, connected to a delicate electrometer. The platinum wire leading to A was protected by earthed guard rings from collecting charges by leakage along the inner or outer surfaces of the glass tube through which it was sealed. A hangs inside a short hollow platinum cylinder, the base of which is of fine platinum gauze B. C and D are two circular pieces of fine platinum gauze which fill the horizontal section of the central tube of the apparatus, as indicated in the diagram. B, C, and D are about 8 mm. apart, while D is about 13 mm. above the filaments. This arrangement of the plate A and of the three platinum grids is similar to that which has been employed by Horton and Davies in their measurements of the critical potentials for the production of radiation from gases. By suitably selecting the values of the electric fields between these grids it is possible to arrange that the electrometer is only deflected by radiation illuminating the plate A

Fig. 2.



or the surrounding platinum cylinder. An arrangement of electric fields which secures this result is indicated diagrammatically in fig. 2. Electrons from the filament F bombard the target T with energy due to a fall through a potential difference  $V_1$  which could be increased up to 230 volts. The lower gauze D was maintained at  $V_2$  volts negative to the filament; C was  $V_3$  volts positive to D,  $V_3$  being always

greater than  $V_1 + V_2$ , so that none of the positive ions which are liberated by the electron bombardment of the target and which pass through the gauze D can travel to the level of C. The experiments of Horton and Davies have shown, however, that such positive ions will liberate electrons from the platinum gauze D when their velocity of impact exceeds a certain small amount (that due to a fall through about 20 volts in the case of the positive ions from platinum). Any electrons so liberated are accelerated by the field  $V_3$  towards the collecting electrode, but are prevented from reaching that electrode by the field  $V_4$  between the gauzes C and B. Any positive ions liberated from C under the bombardment of these electrons could be turned back by the field  $V_5$  between the plate A and the gauze B, but experiment showed that the number of these positive ions was too small to give a detectable effect. The field  $V_5$  was therefore usually kept at a small constant value during the observations, so as to give greater steadiness to the electrometer readings than is obtained if this field is large. By reversing the direction of  $V_5$ , the direction of the photoelectric current between A and B is reversed, thus making it possible to verify that the current measured by the electrometer is due to photoelectric action and does not arise from some spurious ionization effect.

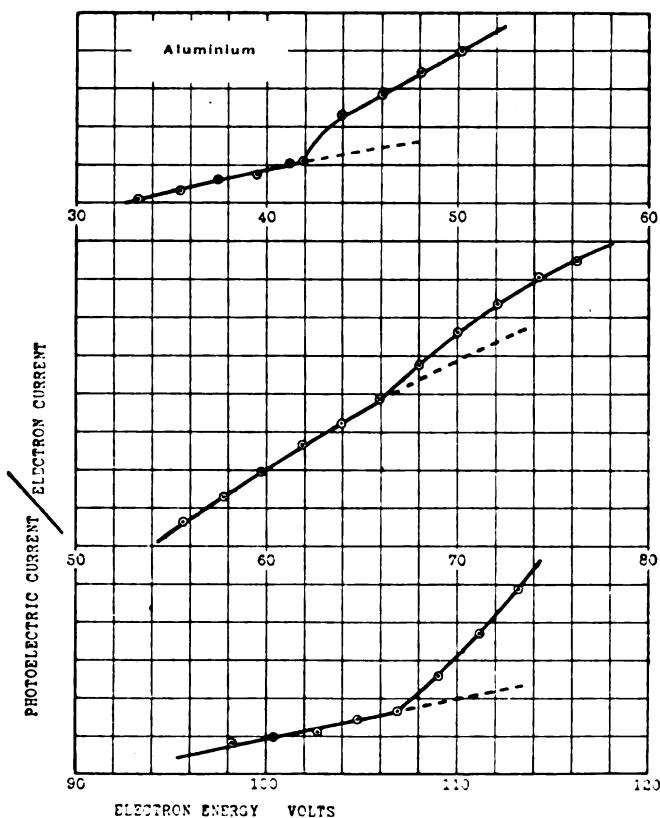
During the measurements of the photoelectric currents with the electrometer the total electron current between the filament and the target was also measured on a galvanometer. In this way a series of values of the photoelectric current per unit bombarding electron current was obtained, and these values were plotted against the corresponding values of the energy of the bombarding electrons. These values were obtained by adding to the various applied potential differences  $V_1$  a small correction determined experimentally in the usual manner.

### *Experimental Results and Discussion.*

Within the limits of electron energies investigated, i. e. up to 230 volts, definite indications of the existence of two critical values for the production of characteristic radiations were found with each of the targets, iron, nickel, copper, and zinc, while in the case of aluminium three critical values were obtained. Radiation was first detected from the targets when the energy of the electron stream was about 11 volts. Whether this first detection of radiation merely indicates the stage at which, with this apparatus, the photoelectric effect of the general impulse radiation (as distinct

from characteristic radiation) becomes measurable, or whether 11 volts correspond to the energy necessary to displace or to remove one of the most loosely attached electrons of the atomic system, is a matter requiring further investigation. Observations were first taken over ranges of about 60 volts at a time. The regions at which indications of bends in the curves were found were then investigated, and the results of some of the curves obtained over these limited ranges are given below.

Fig. 3.



#### *Aluminium.*

Curves showing the three critical voltages for this metal are given in fig. 3. The values deduced for these voltages from several sets of curves are 42, 66, and 107 volts.

Fig. 4 shows the two breaks which were located in the curves for this element, the first being at 73 volts and the second at 166 volts.

Fig. 4.

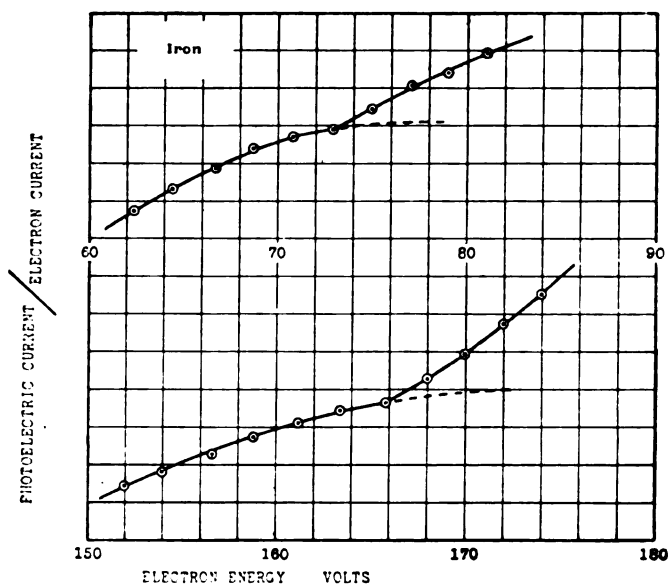
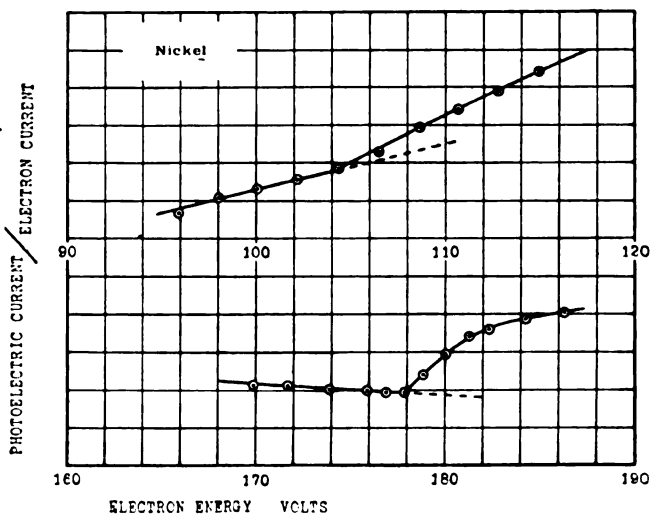


Fig. 5.



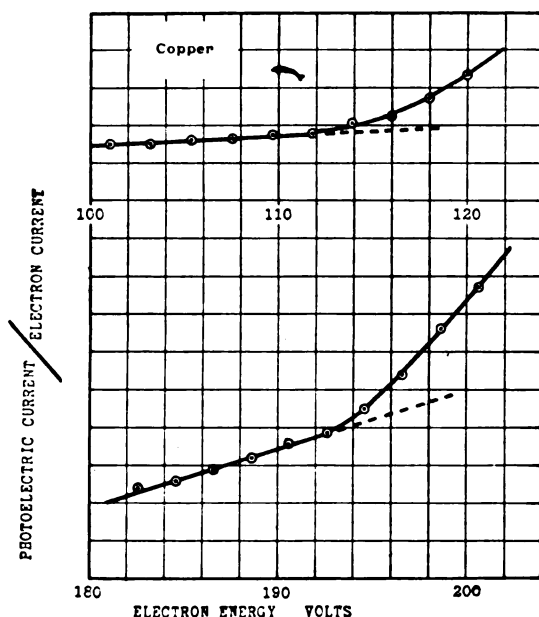
*Nickel.*

For this metal, as shown in fig. 5, discontinuities were found at 104 volts and 178 volts.

*Copper.*

The critical values obtained for this element were 112 volts and 193 volts, as indicated in the curves of fig. 6.

Fig. 6.



*Zinc.*

In the case of zinc the values obtained for the first critical voltage in different experiments varied over a wider range (some 8 volts in the extreme cases) than in the other elements investigated. The value most often obtained was 119 volts, at which point a discontinuity is indicated in the curve of fig. 7. The higher critical point obtained with this metal was at 200 volts.

In order to ascertain with which particular energy level the critical energy values which have been found in this investigation are to be associated, the Moseley curves for the various M absorption limits have been plotted and

Fig. 7.

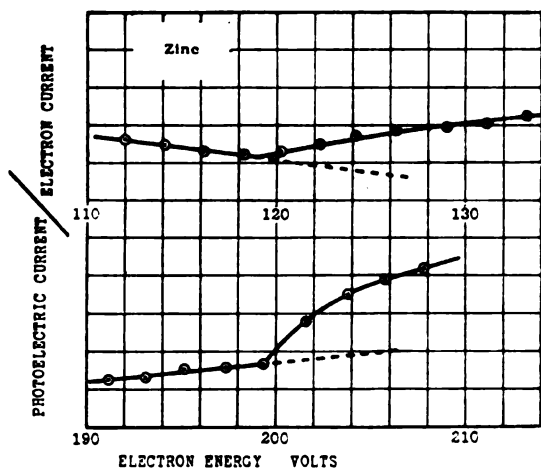
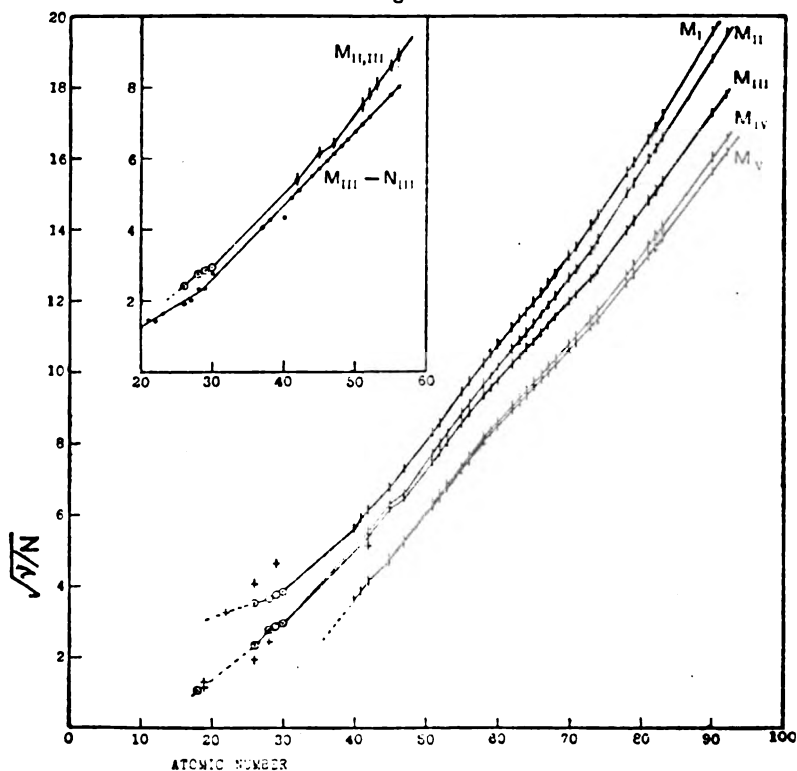


Fig. 8.



prolonged to low atomic numbers (see fig. 8). The square roots of the quantities  $\nu/N$ , where  $N$  is the Rydberg constant and  $\nu$  is the wave number, have been plotted as ordinates and the atomic numbers as abscissæ. Bohr's notation is employed throughout this paper for designating the various energy levels, and in referring to X-ray emission lines use is made of Siegbahn's notation as revised by Coster. The Moseley curves have been plotted for absorption limits rather than for emission lines because, in order to excite the lines associated with any particular level, it is presumably necessary to supply the energy required for the removal of an electron from the appropriate sub-group to the boundary of the atom, or at any rate to the first incomplete outer electronic group. Five M critical absorption wave-lengths have been measured spectroscopically for uranium ( $z=92$ ) and for thorium ( $z=90$ ) and three such wave-lengths for bismuth ( $z=83$ ). Values of the various M critical absorption wave-lengths for elements of lower atomic number can be computed from the frequency relations given below for those cases in which the K and L absorption wave-lengths, and the K and L emission wave-lengths, have been measured directly:—

$$\begin{aligned} M_I &= L_{III} - L_I = L_{II} - L_{\eta}, \\ M_{II} &= K - K_{\beta_3} = L_I - L_{\beta_1}, \\ M_{III} &= K - K_{\beta_1} = L_I - L_{\beta_3}, \\ M_{IV} &= L_{III} - L_{\alpha_2} = L_{II} - L_{\beta_1}, \\ M_V &= L_{III} - L_{\alpha_1}. \end{aligned}$$

L critical absorption wave-lengths have been measured spectroscopically for ten elements between uranium ( $z=92$ ) and tungsten ( $z=74$ ) and for elements between neodymium ( $z=60$ ) and antimony ( $z=51$ ), and the necessary emission lines have been measured for most of these elements.

By using the frequency relations

$$\begin{aligned} L_{II} &= K - K_{\alpha_2}, \\ L_{III} &= K - K_{\alpha_1}, \end{aligned}$$

it is possible to compute the values of L critical absorption wave-lengths from observations of K absorption limits and K emission lines, and by using the values of the L absorption limits thus computed, to calculate the values of  $M_I$ ,  $M_{IV}$ , and  $M_V$  from the relations already given, even in cases where L critical absorption wave-lengths have not been



measured directly. The quantities  $\nu/N$ , and also the square roots of these, for the various M absorption limits have been worked out down to  $z=40$  by Bohr and Coster\*, much of their data being obtained from researches which have recently been carried out in Siegbahn's laboratory by Coster himself and others. These values have been used in plotting most of the curves shown in fig. 8, and points obtained from Bohr and Coster's tables of  $\sqrt{\nu/N}$  are marked in this figure by short vertical lines across the curve. The lines for  $M_{II}$  and  $M_{III}$ , and those for  $M_{IV}$  and  $M_V$ , merge together for low values of the atomic number, as is readily seen. In the case of the  $M_{II,III}$  level, Bohr and Coster give values of  $\sqrt{\nu/N}$  for elements from  $z=29$  to  $z=13$ , but these have not been marked in fig. 8 on account of their being very irregularly situated. Moreover, the accuracy of the computed values for the case of elements of low atomic number seems very doubtful, for if the values obtained for the K absorption limits by different observers are employed, very different values of the M absorption limit result from the computation. The percentage error in the computed value, resulting from a small error in the measurement of the K absorption limit or of  $K\alpha_1$  or  $K\alpha_2$ , is very considerable because the two quantities whose difference has to be taken are so nearly equal for low atomic numbers.

The square roots of the quantities  $\nu/N$  connected by the quantum relation with the critical voltages determined in this investigation for the elements iron ( $z=26$ ), nickel ( $z=28$ ), copper ( $z=29$ ), and zinc ( $z=30$ ) are marked in fig. 8 by circles, and the value of  $\sqrt{\nu/N}$  corresponding to the ionization potential of argon ( $z=18$ ) determined by Horton and Davies† is similarly marked. Values calculated from observations of other investigators, by the excitation potential method, are marked with a cross in fig. 8. The value for molybdenum ( $z=42$ ) was calculated from data obtained by Richardson and Bazzoni‡, and the values for titanium ( $z=22$ ), iron, and copper from experiments by Kurth§. A lower point obtained by Kurth for copper falls slightly below the smaller of the two values obtained by the authors for this element, but is not shown in fig. 8, since it would be indistinguishable from the point already marked. The

\* N. Bohr and D. Coster, *Zeits. f. Phys.* xii. p. 6 (1923).

† F. Horton and A. C. Davies, *Proc. Roy. Soc. A*, xcvii. p. 1 (1920), and cii. p. 131 (1922).

‡ O. W. Richardson and C. B. Bazzoni, *Phil. Mag.* xlii. p. 1015 (1921).

§ *Loc. cit.*

values for potassium ( $z=19$ ), and the value for nickel which is marked with a cross, were obtained by Mohler and Foote\*.

The existence of the gap between the values calculated from spectroscopic data, and the values obtained from excitation potential methods, *i. e.* the gap between  $z=40$  and  $z=30$ , makes it difficult to decide with certainty with which energy level the various values obtained in this research are to be associated. The general trend of the various lines suggests that the lower set of values are associated with the  $M_{II, III}$  level, and that the upper set of values are associated with the  $M_I$  level. To obtain more definite evidence on this matter, however, another line was computed corresponding to  $M_{III}-N_{III}$ , and is shown in the lower of the two curves in the upper left-hand corner of fig. 8. The line was computed from the relations

$$(1) K_{\beta_2} - K_{\beta_1} = M_{III} - N_{III},$$

$$(2) L_{\gamma_3} - L_{\beta_3} = M_{III} - N_{III}.$$

For the elements between  $z=56$  and  $z=37$  the values were calculated from relation (2), using Hjalmar's determinations of the wave-lengths of some of the L emission lines by the precision method†, and Coster's determinations which were made with reference to Hjalmar's lines‡. For the elements  $z=30$  to  $z=20$  the values were calculated from relation (1), using recently obtained data collected by De Broglie§. It may be seen that, with the exception of the value for  $z=40$ , the points for atomic numbers between 56 and 37 lie very nearly on a straight line a little below the  $M_{III}$  line, part of which is plotted again in the same diagram for comparison with the  $M_{III}-N_{III}$  line. The positions of the lower points on this latter line make it clear that the lower set of values obtained in this research for iron, nickel, copper, and zinc cannot be associated with the  $M_{IV, V}$  line, for this line lies below the  $M_{III}-N_{III}$  line while these four points (marked with circles) are above the  $M_{III}-N_{III}$  line, as would be expected if they are to be associated with the  $M_{II, III}$  level.

For comparison with the  $M_I$  curve a line was computed, from  $z=56$  as far as  $z=37$ , corresponding to  $M_I-N_I$  from the relation  $L_{\lambda_5} - I_{\gamma_7} = M_I - N_I$  and Coster's precision data. This line, which, to avoid confusion, is not shown in fig. 8, was just below the  $M_I$  line, and was considerably straighter

\* F. L. Mohler and P. D. Foote, *Phys. Rev.* xviii. p. 94 (1921).

† E. Hjalmar, *Zeits. f. Phys.* iii. p. 262 (1920), and vii. p. 341 (1921).

‡ D. Coster, *Phil. Mag.* xliii. p. 1070 (1922).

§ *Les Rayons X*, p. 92.

than this, and when prolonged to atomic number 30 was above the lower set of points obtained in this research. Since the values for  $M_I$  cannot lie below the corresponding values on the  $M_I - N_I$  curve, it seems reasonable to conclude that the lower set of points obtained in this research cannot be associated with the  $M_I$  level. The  $M_I$  line and the  $M_{II, III}$  line have therefore been prolonged so as to connect with the upper set of ringed points, and with the lower set of ringed points, respectively. The two sets of values obtained in this investigation indicate that the curves do not proceed through the elements zinc, copper, nickel, and iron without suffering an inflexion. They therefore support the view that a change in the constitution of the M group, or in an inner electronic group, occurs in this region. In accordance with Bohr's theory, one would expect to find such an inflexion occurring at the element copper ( $z=29$ ); but the observed points for zinc, copper, and nickel lie very nearly on two parallel straight lines, and the lines only show a clear deviation in passing from nickel to iron. Lack of information with regard to the region  $z=40$  to  $z=30$  makes it impossible to make definite statements with regard to inflexions in this part, but it seems possible that the inflexion occurs at zinc ( $z=30$ ) instead of at copper\*.

It will be seen from fig. 8 that the line for any one level is not straight, or even a continuous curve, but that it can be divided up into a series of approximately straight portions. To a close approximation the wave number of any absorption limit is given by the relation  $\nu = N(z-c)^2 \frac{1}{m^2}$ , where  $c$  is a constant which differs for different levels and  $m$  has successive integral values—*e. g.*, 1 for the K level, 2 for the L levels, 3 for the M levels, and so on. In accordance with this relation, the graph of  $\sqrt{\nu}/N$  against atomic number must be a straight line for any particular level so long as  $c$  remains constant. This quantity can, however, be looked upon as consisting of the sum of two quantities  $c_1$  and  $c_2$ , one of which,  $c_1$ , depends upon the number of electrons in groups of smaller energy value than the one under consideration, and the other of which,  $c_2$ , depends upon the number and arrangement of electrons in the group under

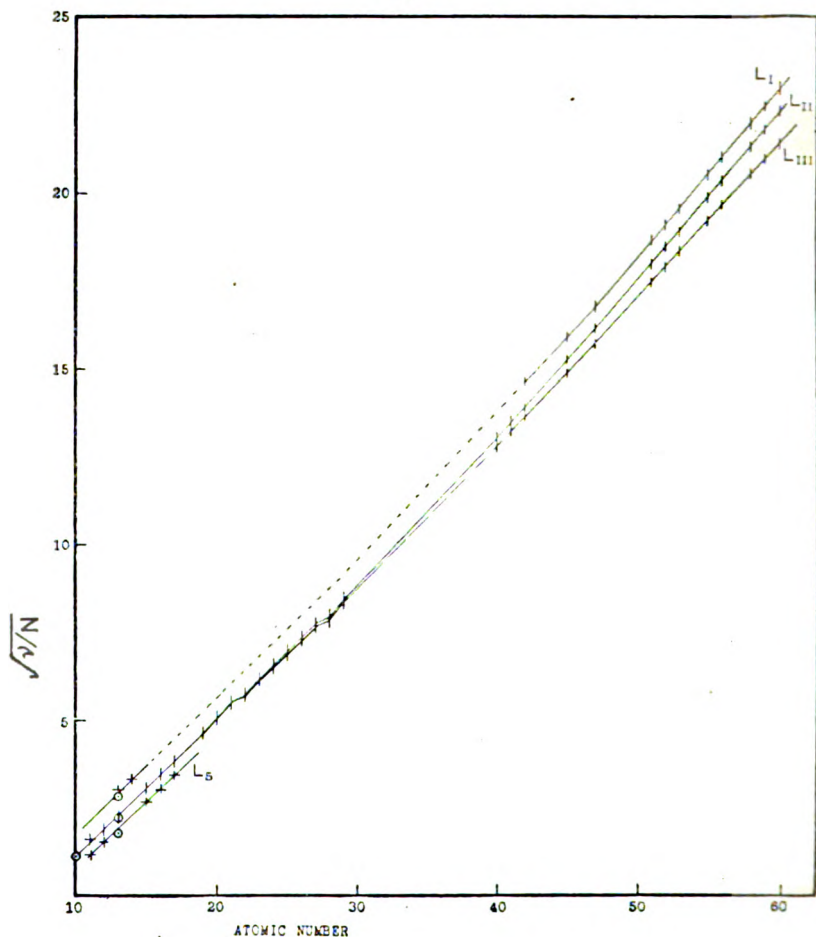
\* Since the communication of this paper, it has been pointed out to the authors by Prof. Bohr and Dr. Coster that the fact that the valency of the elements in this region is not constant may prevent the change of slope in the curve occurring sharply at the element copper and may cause it to occur in a more gradual manner.

consideration, and in outer electronic groups. An increase in the number of electrons in such groups causes an increase in  $c_2$ , this increase being greater if the change is in the number of electrons in the particular group itself than if it is merely in an outer group. Therefore, at any stage where an electronic group is in process of development, the quantity  $c_2$ , and also the quantity  $c$ , corresponding to that group will increase more rapidly with increasing atomic number. The frequency  $\nu$  of the corresponding absorption limit will therefore increase less rapidly with increasing atomic number, and the line should show a less steep portion extending from the element at which the change commences to the element at which the development of the group is complete. The upper parts of the lines given in fig. 8 for the various M levels show less steep portions at stages where, in accordance with Bohr's theory, changes in the constitution of the N group are in progress, this group being linked to a certain extent with the M group. Interpreted in this way, the fact that the lines for the  $M_I$  and  $M_{II,III}$  levels are less steep over the regions titanium to zinc, and nickel to zinc, respectively, than elsewhere, supports the theory that the constitutions of the sub-groups with which these levels are connected are themselves changing in this region.

In accordance with the view that the M group at argon ( $z=18$ ) consists of two sub-groups of four electrons each, while at copper it consists for the first time of three completed sub-groups each of which contains six electrons, the critical values found for argon and potassium must be associated with the  $M_{II,III}$  level. The fact that between iron and nickel on the  $M_{II,III}$  line the slope is considerably steeper than between nickel and zinc, and the fact that there is a steep slope for at any rate part of the way between argon and iron, suggests that the change in the second M sub-group occurs between nickel and zinc, or possibly between cobalt and zinc, but not before cobalt ( $z=27$ ). That the slope of the  $M_I$  line appears to be less between titanium ( $z=22$ ) and zinc ( $z=30$ ) than elsewhere, may be taken to indicate that the change in the constitution of the first M sub-group commences at a lower atomic number than the change in the second M sub-group. It is probable that the irregularities in the slope of the lines between the various points is to be connected with the fact that a change in the constitution of one sub-group commences, and that then a change in the constitution of another sub-group begins before the first change is completed.

In order to ascertain with what absorption limits the values obtained for aluminium are to be associated, the Moseley curves for the various L absorption limits have been plotted downwards from  $z=60$  (see fig. 9), using the values

Fig. 9.



of  $\sqrt{\nu/N}$  worked out by Bohr and Coster. As in the case of the lines for the M absorption limits given in fig. 8, values obtained from the tables are marked by short vertical lines, values determined in this research by circles, while values obtained by other observers using the excitation potential

method have been indicated by crosses. Down to  $z=51$  the critical absorption wave-lengths have been measured spectroscopically for many of the elements. Where the critical absorption wave-lengths have not been measured directly, it is possible to compute them, if the K absorption wave-lengths and the K and L emission wave-lengths have been measured, by using the two relations already given for  $L_{II}$  and  $L_{III}$  and the following for  $L_I$ :—

$$L_I = K - K_{\beta_3} + L_{\beta_1} = K - K_{\beta_1} + L_{\beta_3} = K - K_{\beta_2} + L_{\gamma_3}.$$

The spectroscopic data available enabled Bohr and Coster to determine the values of  $\sqrt{\nu/N}$  as far as  $z=12$  in the case of the  $L_{II, III}$  absorption limit, but only as far as  $z=42$  in the case of the  $L_I$  absorption limit. Apart from observations by the excitation potential method, the only direct information available with regard to the L absorption wave-lengths of elements of low atomic number is that provided by the work of Holweck\*, who located the absorption limits of various elements by measurements of their absorption coefficients for the continuous radiation from a solid target under electronic bombardment. Holweck located an absorption limit for aluminium at a wave-length connected by the quantum relation with the voltage  $64 \pm 2$ †, which agrees with the second critical value, 66 volts, found for aluminium in this investigation. The prolongation of the Moseley curves makes it clear that this critical voltage for aluminium ( $z=13$ ) is to be associated with the  $L_{II, III}$  level, and that the higher value (107 volts) is to be associated with the  $L_I$  level. The values for aluminium and silicon ( $z=14$ ) marked with a cross were found by Kurth, and appear to be associated with the  $L_I$  level also.

The lowest discontinuity which we found in our curves for aluminium at 42 volts corresponds to a value of  $\sqrt{\nu/N}$  which lies below the  $L_{II, III}$  line, and which is therefore to be attributed either to some abnormal state of the L group or to the displacement of an electron from the second L sub-group to one of the M sub-groups instead of to the boundary of the atom. Mohler and Foote have found in the cases of sodium ( $z=11$ ), magnesium ( $z=12$ ), phosphorus ( $z=15$ ), sulphur ( $z=16$ ), and chlorine ( $z=17$ ) similar discontinuities in their current-voltage curves at voltages below those which must be associated with the  $L_{II, I}$  level. Hjalmar‡

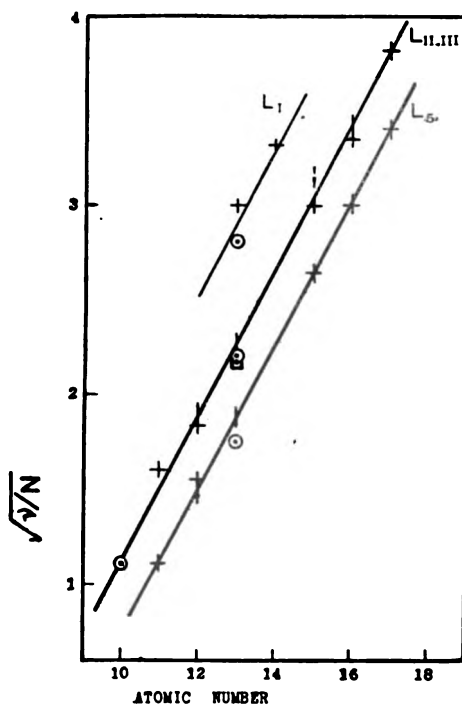
\* M. Holweck, *Comptes Rendus*, clxxiii. p. 709 (1921).

† This point is shown in fig. 10, and is marked with a dot enclosed by a square.

‡ E. Hjalmar, *Phil. Mag.* xli. p. 675 (1921).

found for several elements in this region of atomic numbers, K emission lines which have no parallels in the X-ray spectra of the heavier elements. These lines he designates as  $\alpha_1'$ ,  $\alpha_3$ ,  $\alpha_4$ ,  $\alpha_5$ ,  $\alpha_6$ ,  $\beta_1'$ , and  $\beta'$ . Mohler and Foote associate the values of  $\sqrt{\nu/N}$ , which they obtained from their set of low discontinuities, with the occurrence of these additional lines. Using the relation  $K - K\alpha_3 = L_{\alpha_5}$ , they compute values which when plotted according to the Moseley relation give a line parallel to the corresponding part of the  $L_{II,III}$  line\*. This line is shown in fig. 10, in

Fig. 10.



which diagram the lower parts of the  $L_{II,III}$  line and the  $L_I$  line are drawn again on a larger scale than in fig. 9, the marking of the points being as already described. On the  $L_{\alpha_5}$  line the points computed from the differences  $K - K\alpha_3$  are marked with vertical lines across the curve, the one for sulphur ( $z=16$ ) being coincident with a point plotted from Mohler and Foote's observations. It may be seen that the

\* 'The Origin of Spectra,' p. 208.

values of  $\sqrt{\nu/N}$  connected with Mohler and Foote's voltages lie either on, or very close to, this line. The line  $K\alpha_3$  was observed by Hjalmar in the case of aluminium, and by computing  $L_5$  from the relation given above and ascertaining the voltage connected by the quantum relation with the wave number so determined, the value 49.1 volts is obtained. This value is rather higher than the value (42 volts) which we determined experimentally for aluminium, so that it seems unlikely that our experimental value is to be associated with this hypothetical  $L_5$  limit. Wentzel\* has shown that the additional K emission lines observed by Hjalmar on the short wave-length side of  $K\alpha_1$  are emitted by atoms which have lost more than one electron, and which have therefore absorbed more energy than that corresponding to the ordinary K absorption limit. If this is the case, then by taking the difference  $K-K\alpha_3$  we do not obtain a quantity which has any true physical significance in the sense of an absorption limit. An L absorption limit on the *short* wave-length side of the usual limits might be expected if the simultaneous removal of two electrons from the L group took place, but it is difficult to see how an absorption limit on the *long* wave-length side of  $L_{II,III}$  can be accounted for by such multiple ionization. The value (42 volts) obtained in our experiments must be connected with a genuine absorption limit, and not simply with a quantity which is calculated from the difference between a K absorption limit and a K emission line which corresponds to some exceptional state of the atom.

For the elements titanium ( $z=22$ ), vanadium ( $z=23$ ), and chromium ( $z=24$ ) Fricke† found photographically an absorption discontinuity lying on the long wave-length side of the principal K discontinuity, and it has been suggested by Coster‡ that this anomalous discontinuity is to be connected with the removal of an electron from the K group to one of the incomplete M sub-groups. Such a suggestion receives support, as Coster has pointed out, from the discovery by Hjalmar of an emission line which he calls  $K\beta'$ , which has *exactly* the same wave-length as the anomalous discontinuity. The authors therefore think it probable that the critical stage which they obtained at 42 volts, in aluminium, and the low values found by Mohler and Foote for the elements sodium, magnesium, phosphorus, sulphur, and chlorine correspond to the displacement of an electron within the atom from the second L sub-group to one of the

\* G. Wentzel, *Ann. der Phys.* lxi. p. 437 (1921).

† H. Fricke, *Phys. Rev.* xvi. p. 202 (1920).

‡ D. Coster, *Phil. Mag.* xlv. p. 546 (1922).



incomplete M sub-groups. According to Bohr's theory, the first M sub-group in aluminium contains two electrons and the second M sub-group contains one electron. The question arises as to which of these two incomplete M sub-groups receives the displaced electron at the 42-volt stage. If the electron enters the second M sub-group, we should expect  $L_{II, III} - L_{(anomalous)}$  to be comparable with the ionizing potential of the element of next higher atomic number. The difference between our values for  $L_{II, III}$  and  $L_{(anomalous)}$  is 66 volts—42 volts = 24 volts, however, a value which is considerably higher than the ionizing potential of most elements, so that it seems unlikely that the critical value at 42 volts for aluminium can be accounted for in this way. Moreover, a transition from the second L sub-group to the second M sub-group would not be in accordance with the selection principle, since the azimuthal quantum numbers of these two sub-groups are the same. It would appear then, that 42 volts corresponds to the energy necessary for the removal of an electron in the aluminium atom from the second L sub-group to the first M sub-group\*.

### *Summary.*

Investigations of the voltages connected with some of the longer wave-length absorption limits have been made for the elements aluminium, iron, nickel, copper, and zinc by the excitation potential method. The following critical values have been obtained :—

For aluminium...	42 volts, 66 volts, and 107 volts.
„ iron .....	73 volts and 166 volts.
„ nickel.....	104 „ „ 178 „
„ copper .....	112 „ „ 193 „
„ zinc ... ..	119 „ „ 200 „

By extrapolating the Moseley curves for the various absorption limits to low atomic numbers, the lower of the two

\* It has been pointed out to the authors by Prof. Bohr and Dr. Coster that for elements of atomic number below about 24 the values of  $\sqrt{Z/N}$  for  $L_{II, III}$  given in their tables cannot be relied upon to the same extent as the values for higher atomic numbers, on account of the various electrical conditions of the atoms in the different compounds used in the experiments from which the data for the calculation were obtained. The possibility that the critical value of 42 volts for aluminium should be associated with the  $L_{II, III}$  level, and the critical value 66 volts with the  $L_I$  level, while the highest value should be associated with some doubly ionized condition of the aluminium atom, cannot, therefore be entirely ruled out on the evidence at present in existence.

values obtained for each of the metals, iron ( $z=26$ ), nickel ( $z=28$ ), copper ( $z=29$ ), and zinc ( $z=30$ ), was found to be associated with the  $M_{II,III}$  level, and the higher of the two values obtained for each of these elements was found to be associated with the  $M_I$  level. The changes in the slope of the  $M_I$  and  $M_{II,III}$  curves in passing through the observed points support the view that a change in the constitution of the M electronic group is in progress as we pass from one of these elements to another. The results suggest that the development of the second M sub-group from four electrons to six electrons, as required by Bohr's theory, does not commence before the element cobalt ( $z=27$ ), but that the similar development of the first M sub-group commences for a lower value of the atomic number.

By extrapolating the Moseley curves for the L absorption limits in a similar way, the two higher values found for aluminium have been connected with the  $L_I$  and  $L_{II,III}$  levels respectively. From analogy with the anomalous K absorption limits found by Fricke for titanium, vanadium, and chromium, which Coster suggests are due to the displacement of an electron from the K group to an incomplete M sub-group, it seems probable that the lower value (42 volts) found for aluminium is to be associated with the displacement of an electron from the second L sub-group to the first M sub-group.

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LXXXIV. *Vacuum Grating Spectrograph and the Zinc Spectrum.* By R. W. WOOD, *Professor of Experimental Physics, Johns Hopkins University* \*.

[Plate XI.]

THE reproductions of spectrograms obtained with concave gratings mounted in vacuum spectrographs which have been published during the past five years appear to indicate that higher resolving power in the short wave-length region is very much to be desired, if accurate determinations of wave-length are to be made.

During the past winter I have made some preliminary investigations with two instruments of this type which have been constructed in the shop of the University.

In view of the present grating situation it appears to be worth while to publish a brief statement of what may be

\* Communicated by the Author.

expected of short-focus concave gratings, which can now be produced on the Rowland engines as desired.

A good deal of time was spent in getting the spectrograph into proper condition, as much trouble was found owing to the presence of absorbing vapours, and at the close of the University year but two satisfactory spectrograms had been obtained, one of carbon and one of zinc, with carbon as an impurity. The lines on these two plates, however, were sharper than any that I have ever seen, and the focus appeared to be perfect over the entire range of the plate.

A three-fold enlargement of the zinc spectrogram is reproduced in Plate XI. *a* in coincidence with a corresponding portion *b*, of the spectrum enlarged to the same scale from the reproduction accompanying Sawyer's paper on the Zinc spectrum, published in the 'Astrophysical Journal' for December 1920.

Certain groups of lines, enlarged 7.5 times, are reproduced at *c*, and immediately above these, small regions of these groups, enlarged 34 times, are given. It is only in these last that the lines show a width comparable with the width of the lines in Sawyer's spectrum. The corresponding portions of spectrum, in the series of enlargements, are indicated by brackets. This spectrum will be discussed more fully presently.

### *The Spectrograph.*

The spectrograph was constructed along lines similar to those indicated in Prof. McLennan's paper, published recently in the Proceedings of the Royal Society. Certain modifications, intended to facilitate the operation and adjustments of the instrument, were introduced, but will be passed over without comment, as, in the opinion of the writer, the best type of vacuum spectrograph is yet to be designed. Through a misunderstanding on the part of the mechanic, the large conical ground joints were put together with alcoholic shellac, the vapour from which was doubtless responsible for the failure of the instrument to record anything below wave-length 1600 for several weeks. With continued operation, however, the range gradually increased until a group of lines at 834 appeared, the limit obtained up to the present time. With more rapid methods of exhaustion, however, and continued operation, matters will undoubtedly improve. Up to the present time I have given but little attention to the design of the instrument, being occupied

chiefly with the question of the best type of grating to employ. Thus far but one grating has been ruled, but as it appears to yield spectra of high quality with comparatively short exposures, a brief description of it may not be out of place.

### *The Concave Grating.*

Owing to the difficulties found in securing a sufficiently constant temperature in the dividing-engine room, practically no gratings have been ruled on the Rowland machines since the removal of the Physical Laboratory to its temporary quarters in the Electrical Engineering Building six years ago. The walls of the small room are exposed to the outer air on two sides, and the gas-heated radiator controlled by a thermostat was found to be useless, as the flame was frequently blown out by air blasts from outside.

Having need of a short-focus grating for a recently constructed vacuum spectrograph, I took up the problem of securing proper conditions for ruling last autumn. The gas radiator was removed, and the inlet and exhaust pipes through the wall closed. In its place was installed a small gas stove of sheet iron, heated by a ring of small bat-wing burners. This type of flame was chosen in preference to the bunsen flame, as it can be turned down indefinitely without snapping back. The stove was provided with a chimney of sheet iron about 12 feet long, which passed out through the wall into the corridor. The gas supply was regulated by a toluene thermostat, the rising mercury column closing a glass tube perforated with a very minute hole a little above its open end. This hole served as a by-pass for gas in sufficient quantity to maintain flames about 2 cms. in height, furnishing enough heat to keep the room several degrees above that of the outside air in the warmest weather.

This arrangement has given perfect satisfaction, the temperature in the room having held constant to within  $0^{\circ}.2$  throughout the winter and spring. Except when sudden and extreme temperature changes occurred outside, the changes in the room were not over  $0^{\circ}.1$ .

While this is satisfactory for short-focus gratings of moderate resolving power, a better control was desirable for ruling very large gratings of high resolving power. To meet this requirement a large grid of very fine insulated resistance wire was set up in the glass cage in which the

engine operates. The heating of this grid by a 110-volt current is so slight that it cannot be felt by the fingers. A toluene thermostat will control the current, and judging from results found in controlling the temperatures of gratings during long exposures, I feel sure that the engine can be operated continuously at a temperature which is constant to within  $0^{\circ}01$ .

From a number of trial rulings a setting of the diamond was selected which gave a light brown colour in the central image, and a symmetrical distribution of the light in the spectra to the right and left. Professor Millikan has stated that he believes that the rulings best suited for work in the Lyman region are made with so light a touch that some of the original polished surface is left undisturbed. I was unable, however, to convince myself by examination with a  $\frac{1}{2}$  inch immersion objective and vertical illumination that such was the case, except in one instance where the ruling was so light that markings were left by the diamond only on the softer crystals of the mosaic of which the speculum alloy is made. Such rulings were obviously unfit for use, and I accordingly chose one not much lighter than those usually employed. The microscope gave no indication that any of the original surface of the concave plate remained, and there was no marked concentration of light in any one spectrum.

The radius of curvature of the plate was one metre, and it was ruled with 15,000 lines to the inch, the ruled surface measuring about  $1 \times 4$  inches.

The exposure times required with this grating were not longer than those recorded by other investigators working under similar conditions.

### *The Electron-Arc.*

The source of light employed was the peculiar type of discharge which I described somewhat fully in 1897\*.

In this paper it was shown that an intermittent arc-like discharge could be made to pass between two beads of platinum or other metal, separated by a distance of about 1 mm., if a source of high potential with a spark-gap in circuit was employed. It was found that the anode was rapidly eaten away, the spherical bead eventually becoming

\* R. W. Wood, "A new type of Cathode discharge and the production of X-rays, together with some notes on diffraction," *Physical Review*, July 1897.

hemispherical in form, while a deposit of the metal was built up on the cathode. The surface of the anode upon which the arc played was found to be a very powerful source of X-rays, the intrinsic intensity being from 10 to 20 times as great as that from the focus tubes available at the time, the bones of the arm showing distinctly in a fluoroscope with a radiating source of about one square millimetre.

From a study of the source of the X-radiation by pinhole photography, I came to the conclusion that the cathode rays, which went off in all directions from the negative ball and wire when no spark-gap was included, were, by the introduction of the gap, gathered into a dense bundle between the ball electrodes, but that a few escaped and played around the ball, impinging upon the supporting wire almost, if not quite, down to the point at which the wire joins the ball. This type of discharge has been subsequently observed and studied by other investigators, and is usually referred to as the "hot-spark." I suggested its use on several occasions many years ago as a promising method of obtaining metallic spectra in the region of very short wave-lengths, but having no vacuum spectrograph, I never put it to this use. Professor Millikan has, however, employed it in this way, with most brilliant results, as is well known. The new Lilienfeld X-ray tube appears to operate on a somewhat similar principle. In this tube a pointed cathode is mounted at a distance of a millimetre or two from a concave anode in a very high vacuum. The electrons are drawn out of the pointed cathode in a dense stream by the very strong electric field, and raise the anode cup to a white heat. The discharge itself, however, is non-luminous in this case, I am told.

In the present instance the discharge was operated by a 30,000-volt transformer, with two large leyden-jars and a spark-gap of about a centimetre. Discharges of very brief duration only were employed, as continued operation caused too great an evolution of gas for the slow exhaustion through the slit to take care of, and resulted in a diffuse glow discharge which filled the small bulb in which the electrodes were mounted. The short flashes were obtained by striking the primary wires of the transformer together at intervals of about one second, the time of contact being so brief that only a single flash occurred. About 1000 flashes gave a fully exposed plate, and required only about twenty minutes. Schumann plates made by the Hilger Co. were employed.

*Discussion of the Spectra.*

With a grating of only one metre radius a very fine slit must be employed, and the focus determined to within 0.5 mm. to secure the best results. It does not appear as if anything could be gained by the use of a bent plate.

If we compare the spectrum reproduced in Plate XI. *a*, with the zinc spectrum published by Sawyer (*h*), the first thing that strikes our attention is the relative weakness of the latter in the region around 1500. My plate shows a very strong triplet at 1500, no trace of which is given by Sawyer's plate. This line is not a true triplet in all probability, and its origin is unknown, though the two stronger members agree closely in position with two Silicon lines on one of Prof. Fowler's photographs. The zinc rods which I used were not chemically pure, though of better quality than ordinary battery rods.

My plate shows a far greater number of lines than Sawyer's, and I believe that most of them are due to zinc.

In the region between  $\lambda = 1283$  and  $\lambda = 1500$  are recorded 96 lines against 14 in Sawyer's table.

The carbon line 1036.1 given by Sawyer is, on my plate, a clearly separated doublet, 1037.14 and 1037.50 (Simeon's determination of wave-length).

It seems probable that the weak region on Sawyer's plate around 1500 was due to the presence of some absorbing vapour in his spectrograph. My plate is very weak between 980 and 1240, while Sawyer's shows a very strong group of lines in this region. I find faint records of all of Sawyer's lines between 976 and 1066, but no trace of the 10 lines which he gives between 1066 and 1165. All of the lines of longer wave-length given by Sawyer appear on my plate. It seems evident that absorbing vapour must have been present in both instances, alcohol probably in my case.

The 7.5-fold enlargement of portions of the original spectrogram were made with a microscope fitted with a 16 mm. objective: the 34-fold enlargements were made with a 4 mm. objective. Comparison of these last with Sawyer's spectrogram indicates that the lines on his plate were about 12 times as wide as mine.

He gives, in his table of wave-lengths, the carbon triplet, resolved by Simeon in the second order spectrum (1561.32, 1560.67, 1560.16) as a single line of wave-length 1561.1. My plate shows it as a doublet, with components of equal

intensity and a separation of one Ångström unit. This I cannot reconcile with Simeon's observation, as he gives his lines intensity values of 8, 9, 9, and separations of 0.65 and 0.51.

Simeon's paper on the carbon spectrum in the extreme ultra-violet was published in the *Proc. Roy. Soc.* vol. 102, p. 717. He photographed the zinc lines of the second order spectrum in coincidence with the iron comparison spectrum of the first order, obtaining in this way a far higher degree of precision in his wave-length determinations than in the cases in which the position of lines with reference to the central image is measured.

I was in hopes that, by using Simeon's carbon lines as standards, a fairly accurate table of wave-lengths could be prepared of the zinc lines shown on my plate, on which carbon appears as an impurity. After measuring both my carbon and zinc plates twice, and spending several days on the computations, I have decided, however, to wait until other spectrograms, using pure substances, have been obtained. The spectrum is not quite normal and there are too few carbon lines on my zinc plate, except in the region between 1000 and 1300, for the proper determination of the corrections to be applied.

My carbon and zinc spectra are also not quite on the same scale, due probably to the fact that the temperature of the instrument was not the same in both cases. This makes it impossible to calibrate my zinc plate, with its few carbon lines, from the carbon plate with many lines. Sawyer's table does not include the very strong carbon double line 1335.66, 1323.79 (one of the strongest on my plate), though he finds numerous lines of less intensity. This line, however, lies in the region in which his spectrum is very weak, while mine is very strong at this point. If the absorption spectrum of the vapour in his spectrograph was discontinuous, *i. e.*, channelled like the spectrum of benzine, it might suppress some very strong lines and pass others of less intensity.

I feel quite sure that an accuracy of .05 Ångström will be possible with plates made with proper precautions, that is, assuming Simeon's values of the carbon lines to be correct to this order of accuracy, which I believe to be the case. The error involved in the settling of the cross-hair on the lines of my plate, when translated into wave-lengths, amounted to only 0.03 Ångström, and lines separated by 0.3 Ångström were resolved without difficulty.



While determinations of wave-lengths for the entire spectrum must be deferred until more satisfactory comparison spectra have been secured, I will give a short table of the values found in the region between 1600 and 1930, where practically all of the lines agree in position with lines found by Sawyer with pure zinc, and in addition the lines in the region between 1000 and 1300, where the accuracy is somewhat greater. I believe that all of the values are correct to 0.1 Ång. Sawyer's values are given in a parallel column, together with a column of differences.

TABLE I.

Int.	Zinc λs.		Dif.
	(Wood).	(Sawyer).	
0	1918.67	1919.6	+ .93
0	1863.96	1864.4	+ .44
4	1839.21	1838.8	- .41
1	1833.54	1833.3	- .24
1	1822.05		
0	1811.18	1811.10	- .18
0	1808.23		
6	1767.79	1767.5	- .29
1	1754.04	1753.4	- .64
8	1749.87	1749.4	- .47
6	1707.18	1706.3	- .88
2	1695.49	1695.4	- .09
7	1688.72	1688.5	- .22
10	1673.21	1672.7	- .51
0	1657.86		
1	1657.26		
00	1656.61		
	Carbon.		
7	1651.94	1651.5	- .44
8	1645.05	1644.7	- .35
9	1639.54	1639.1	- .44
9	1629.43	1629.3	- .13
7	1622.87	1622.8	- .07
6	1620.01	1619.6	- .41
6	1601.15	1601.4	+ .25

Assuming my values to be correct to the order of 0.1 Ångström, the errors in Sawyer's table show a maximum value of  $\pm 0.1$  Ång., which seems to be about what is to be expected, in view of the fact that his lines were about ten times wider than mine; this, of course, is on the assumption that his measurements were made from the plate which was reproduced with his paper, which may not have been the case.

The following values were obtained further down the spectrum :—

TABLE II.

Int.	Wood.	Sawyer.	Dif.
2	1307.32		
5	1306.50	1306.1	+ .40
0	1304.71		
2	1303.55		
1	1301.20		
0	1298.47		
1	1296.59		
2	1295.28		
3	1292.21	1293.3	-1.09
0	1291.84		
0	1289.98		
00	1284.58		
00	1283.54	1282.9	+ .64
00	1281.35		
0	1280.34		
00	1278.91		
0	1277.03		
0	1276.24		
1	1274.41		
2	1272.88	1273.1	
2	1272.06		
00	1270.76		
0	1268.15		
3	1265.63	1264	+1.63
3	1262.68		
3	1253.29	1252.5	+ .79
00	1250.24		
00	1249.89		
2	1247.2 Carb.		
3	1228.34	1228.6	- .26
0	1223.41	1223.1	+ .31
0	1215.51 Hydrogen.	1215.9	- .39
0	1204.26		
0	1203.65	1201.5	
0	1200.63		
0	1195.21	1194.6	+ .61
0	1066.3 Carb.		
5	1048.86	1048.8	+ .06
8	1036.84 Carb.	1036.1	+ .74
0	1028.57	1029.8	-1.23
6	1010.11 Carb.	1009.3	+ .81
0	1001.58	1001.2	+ .38
0	834.21		
0	833.08		
0	832.73		

The degree of accuracy of the wave-lengths given in this table may be inferred from the value found for the hydrogen line 1215.51. Simeon gives it as 1215.53.

The carbon line 1010.11 was also a calculated value : Simeon's value is 1010.09.

The region given in this table is the one which is extremely weak on Sawyer's spectrogram, and the fact that he finds

## 750 *Vacuum Grating Spectrograph and Zinc Spectrum.*

but two of the three strong lines 1265, 1262, and 1253 may be perhaps taken as evidence that the absorption band of the vapour in his spectrograph was discontinuous. Additional evidence of discontinuous vapour absorption is given by my plates.

The carbon quadruple line at 1657, which Simeon finds of the same intensity as the triple line at 1560, appears on my plate of the carbon spectrum as a triple line of intensity greatly inferior to that of a double line at 1560. On the zinc plate, however, the triplet is recorded, but there is no trace of the doublet. It seems quite probable that the vapours given off by the electron-arc in the two cases may have shown a different selective absorption. With the arrangements for pumping employed, these vapours entered the spectrograph through the slit. This will be avoided in future work.

### *Lyman Ghosts.*

Some results obtained in the early part of the work, while adjusting and focussing the grating with the aluminium spark as a source of light, led me to take up a study of the Lyman Ghosts shown by the grating. These appear in the region between 1200 and 2000 of the first order spectrum when the spectroscope is filled with air. They are attributed to a periodic error of the order of magnitude of the distance between five or six lines of the grating. Apparently only spectra of higher order than the fifth or sixth were produced by this periodicity, for no trace of the ghosts appeared in the vicinity of the central image.

No trace of them can be seen with visible light, when the quartz mercury arc in combination with a green screen is viewed in the grating, and no trace appears on photographs made with a one-hour exposure with the quartz arc screened with nickel oxide glass, which transmits Hg 3660 at nearly its full intensity.

With an exposure of 1 hour with a naked quartz Hg arc, cooled by water, which emits the 2536 radiation with a terrific intensity, faint traces were secured, while a one-minute exposure to the light of the aluminum spark brought them out strongly.

All of these circumstances, taken together, make me feel that there is still something to be found out in regard to the causes operating in the production of the Lyman Ghosts, the study of which will be continued in the autumn, with different types of monochromatic sources, and with gratings in the ruling of which the driving power of the motor is transmitted to the ruling engine in different ways.

LXXXV. *The Stark Effect for Strong Fields.*

*To the Editors of the Philosophical Magazine.*

GENTLEMEN,—

THE appearance in your May issue of a letter by Mr. H. O. Newbould dealing with two recently-published papers of mine\* on the Stark Effect for Strong Fields, makes it necessary that the details of the correct solution, roughly indicated in my second paper, should be published. The following are the main steps of the analysis with the same notation as before, except where it is specified to the contrary, corresponding equations being denoted by the same numbers:—

As pointed out in the second paper, equation (7) should assume the form

$$B = -\sqrt{A} \left( \sqrt{C + \frac{nhi}{\pi}} \right) + \frac{D}{4A} \left( C - \frac{3B^2}{A} \right) + \frac{5BD^2}{16A^3} \left( 3C - \frac{7B^2}{A} \right), \quad \dots (7)$$

where one of the suffixes 1 or 2 may be attached to the set of letters (A, B, C, D, n), the eight quantities  $A_1, A_2, \dots, D_1, D_2$  being given by equations (5a) and (5b) of the first paper, and  $n_1, n_2$  being quantum numbers.

Equations (12) and (13) should also read

$$\overset{0}{B^2} = A_0 \left( \sqrt{C + nhi/\pi} \right)^2, \dots \dots \dots (12)$$

$$\overset{1}{B^2} = A_0 \left( \sqrt{C + nhi/\pi} \right)^2 \mp \frac{h^4(n_1 + n_2 + n_3) \sqrt{A_0 N}}{32m_0 e E^2 \pi^4} \left( \sqrt{C + \frac{nhi}{\pi}} \right) F, \quad \dots \dots (13)$$

where the notation 0, 1, ... etc. placed above the quantity refers to 0, 1st, ... etc. orders of approximation in the field F respectively. And on substituting for B in the last two terms of (7) from (13) and (12) respectively, we have

$$B = -\sqrt{A} \left( \sqrt{C + \frac{nhi}{\pi}} \right) \mp \frac{m_0 e F}{4A} \left\{ C - \frac{3A_0}{A} \left( \sqrt{C + \frac{nhi}{\pi}} \right)^2 \right. \\ \left. \pm \frac{3h^4(n_1 + n_2 + n_3) \sqrt{A_0 N F} \left( \sqrt{C + \frac{nhi}{\pi}} \right)}{32m_0 e E^2 \pi^4 A} \right\} \\ - \frac{5m_0^2 e^2 F^2}{16A_0^{\frac{5}{2}}} \left( \sqrt{C + \frac{nhi}{\pi}} \right) \left\{ 3C - 7 \left( \sqrt{C + \frac{nhi}{\pi}} \right)^2 \right\}, \quad (14)$$

\* Phil. Mag. xliii. p. 943 (1922), and xliv. p. 371 (1922). These will be referred to as the "first paper" and "second paper" respectively.

or on adding corresponding sides of the two equations embodied in this :

$$\begin{aligned}
 m_0 e E = & -\sqrt{A} \frac{(n_1 + n_2 + n_3) \hbar i}{2\pi} \\
 & + \frac{3m_0 e A_0}{2A^2} \frac{\hbar^2 (n_2 - n_1)(n_1 + n_2 + n_3)}{(2\pi)^3} F \\
 & - \frac{3i\sqrt{A} \hbar^5 N (n_1 + n_2 + n_3)^2}{8 \times (2\pi)^5 E^2 A^2} F^2 \\
 & - \frac{5m_0^3 e^2 F^2 \hbar^3}{8 \times (2\pi)^3 A_0^{5/2}} (n_1 + n_2 + n_3) R, \quad (15)
 \end{aligned}$$

where \*

$$R = \frac{1}{2} (n_1 + n_2 + n_3)^2 + \frac{1}{2} (n_2 - n_1)^2 - \frac{3}{2} n_3^2. \quad (15a)$$

We proceed to solve for A by putting

$$A = -(K + LF + MF^2), \quad . \quad . \quad . \quad (16)$$

so that

$$\left. \begin{aligned}
 \sqrt{A} &= i\sqrt{K} \left( 1 + \frac{1}{2} \frac{L}{K} F + \frac{1}{8} \frac{4MK - L^2}{K^2} F^2 \right) \\
 &\quad \text{approximately,} \\
 \frac{1}{A^2} &= \frac{1}{K^2} \left( 1 - \frac{2L}{K} F \right) \\
 &\quad \text{,,}
 \end{aligned} \right\} \quad (17)$$

And on equating the coefficients of powers of F on the two sides of (15) respectively,

$$\left. \begin{aligned}
 m_0 e E &= \frac{\hbar \sqrt{K}}{2\pi} (n_1 + n_2 + n_3), \\
 0 &= \frac{\hbar L (n_1 + n_2 + n_3)}{2(2\pi) \sqrt{K}} - \frac{3m_0 e \hbar^2 (n_1 + n_2 + n_3) (n_2 - n_1)}{2(2\pi)^2 K}, \\
 0 &= \frac{(n_1 + n_2 + n_3) \hbar}{8 \times (2\pi) K^{3/2}} (4MK - L^2) \\
 &\quad + \frac{3m_0 e L (n_2 - n_1) (n_1 + n_2 + n_3) \hbar^2}{(2\pi)^2 K^2} \\
 &\quad + \frac{3(n_1 + n_2 + n_3)^2 \hbar^5 N}{8 E^2 (2\pi)^5 K^{3/2}} - \frac{5m_0^3 e^2 \hbar^3 (n_1 + n_2 + n_3) R}{8 \cdot (2\pi)^3 K^{5/2}},
 \end{aligned} \right\} \quad (17a)$$

\* This function R is here introduced in order to facilitate comparison with Mr. Newbould's analysis.

giving

$$K = \frac{(2\pi)^2 m_0^2 e^2 E^2}{(n_1 + n_2 + n_3)^2 h^2}, \quad \dots \quad (18)$$

$$L = \frac{3h^2}{(2\pi)^2 E} (n_2 - n_1)(n_1 + n_2 + n_3), \quad \dots \quad (19)$$

$$M = \frac{L^2}{4K} - \frac{6m_0 e h L}{(2\pi) K^{3/2}} (n_2 - n_1) - \frac{3h^4 N (n_1 + n_2 + n_3)}{4 \times (2\pi)^4 E^2 K} \\ + \frac{5m_0^2 e^2 h^2}{4(2\pi)^2 K^2} R, \quad \dots \quad (20)$$

and after some reduction

$$M = \frac{h^8 (n_1 + n_2 + n_3)^4}{4 \times (2\pi)^6 (m_0 e E^2)^2} \left[ 5R - 63(n_2 - n_1)^2 - \frac{3N}{n_1 + n_2 + n_3} \right]. \quad (21)$$

And, further, on using (15 a) and the identity (quoted in the second paper) for N, viz.

$$N = (2n_1 + n_3)(6n_2^2 + 6n_2 n_3 + n_3^2) \\ + (2n_2 + n_3)(6n_1^2 + 6n_1 n_3 + n_3^2) \\ \equiv 3(n_1 + n_2 + n_3)^3 - 3(n_1 + n_2 + n_3)(n_2 - n_1)^2 \\ - n_3^2(n_1 + n_2 + n_3).$$

We have for the energy W the expression

$$W = - \frac{(2\pi)^2 m_0 e^2 E^2}{2(n_1 + n_2 + n_3)^2 h^2} - \frac{3h^2 F}{2(2\pi)^2 m_0 E} (n_2 - n_1)(n_1 + n_2 + n_3) \\ - \frac{h^6 F^2}{16(2\pi)^6 m_0^3 e^2 E^4} N', \quad \dots \quad (23)$$

where N' is given by

$$N' = 10R - 126(n_2 - n_1)^2 - \frac{6N}{n_1 + n_2 + n_3} \\ = (n_1 + n_2 + n_3)^4 \{ 17(n_1 + n_2 + n_3)^2 - 3(n_2 - n_1)^2 - 9n_3^2 \}. \quad (22)$$

This is the result quoted in the second paper.

The Manor House,  
Alphington, nr. Exeter,  
July 9th, 1923.

Yours faithfully,  
A. M. MOSHARRAFA.

LXXXVI. *On Eddies in Air.* By HIRATA NISI and  
ALFRED W. PORTER, *D.Sc., F.R.S., F.Inst.P.\**

[Plate XII.]

**T**HE following investigations were begun by one of us before the war, but preliminary observations only had been taken when the work had to be suspended.

The turbulent motion of a viscous fluid through a pipe has been studied by many investigators, including Osborne Reynolds, the late Lord Rayleigh, Rücker, Stanton; but there is no complete mathematical solution for the motion of a viscous fluid past a solid obstacle, especially when the motion is so fast that eddies are produced. Such solutions as have been given neglect the effect of inertia terms; for example, those of Stokes †, Oseen ‡, Williams §. They can hold therefore only when the velocity is small and the viscosity is great.

There are many papers ‖ dealing with eddies behind an obstacle, and no doubt there are others which have not yet been published; most of them refer to liquids only.

Although the law of dynamic similarity holds independently of the particular fluid concerned (water, air, etc.), we should bear in mind that when there are very great differences in the properties (density, viscosity, etc.) of the fluids compared, the *approximate* law that may have been found to be sufficiently good for one case may be inapplicable to another.

The present paper is concerned with the eddies which form in air which flows past obstacles of various forms; it is divided into three parts.

The first deals with the relations between the dimensions of the obstacles and the critical velocities at which eddies begin to form when the air flows through an air-channel containing the obstacle. Smoke drawn through with the air was used as an indicator. The second deals with the velocity distributions in the eddies and surrounding fluid. Thirdly,

\* Communicated by the Authors.

† Lamb, 'Hydrodynamics,' pp. 591, 596 (1916).

‡ Williams, *Phil. Mag.* xxix. p. 525 (1915).

§ Lorentz, *Ab. ü. Theoretische Physik*, xxxix. (1907).

‖ Ladenburg, *Ann. d. Phys.* xxiii. p. 447 (1907); Bénard, *C. R. cxlvii. p. 839* (1908); Mallock, *Proc. Roy. Soc. A.* lxxxiv. p. 482 (1910-11); Kármán & Rubach, *Phys. Zeitsch.* xiii. p. 49 (1912); Föppl, *Münch. Sitzungsab.* p. 1 (1913); Nayler & Frazer, Reports and Memoranda of Advisory Committee for Aeronautics, No. 332 (1917).

the relation between the mean velocities of flow and of the positions of the eddy-centres was obtained.

The general arrangement of the apparatus is as follows:—

Water from the mains flows into an eleven-litre vessel displacing the contained air which flows successively through a vessel where it picks up smoke and a U-tube (immersed in water) where its temperature becomes equalized. It then enters the air-channel in which the obstacle is mounted. Two sizes of square-sectioned channel were employed, both of brass. The larger one measured  $2.6 \times 2.6 \times 30$  cm., the smaller was  $2.0 \times 2.0 \times 25$  cm.

The method of examination was the same as in ultramicroscopy. In the middle of the brass channel small windows were cut and covered with thin glass plates. Light from a lantern could thus be passed horizontally across the obstacle, and the scattered light examined from above on a camera screen; or alternatively, photographs of the scattered light were obtained. Extensions were put on at each end of the chamber, and at the end of the inlet a piece of gauze inserted to make the stream as uniform as possible. The obstacle was mounted on a wooden plug, which was inserted through a hole in the bottom of the chamber; this plug was rotated in each case until the most symmetrical eddies were formed.

Suitable lenses were used to focus the light, one of them being a cylindrical lens to spread it out into a horizontal sheet in the axial plane of the channel in the neighbourhood of the obstacle. Heat filters were employed to minimize the heating effect.

The camera was furnished with a microscope objective of 2.5 cm. focal length. The image obtained was examined on the focussing screen by means of a simple magnifier; and when suitably steady figures formed by the smoke particles were obtained, the screen could be replaced by a photographic plate and a photograph was taken. But in many cases eye observations only were necessary.

## PART I.

### *The relations between the dimensions of the obstacles and the critical velocities.*

The obstacles employed were:—

A. *Spheres*: steel ball-bearings of nine different sizes, ranging from 1.59 to 7.94 mm. diameter. These were attached to fine embroidery-needles (diameter = 0.34 mm.) which served



as supports; only the smallest necessary amount of solder being used. The spheres as mounted were adjusted to the axial plane of the chamber; care was taken to adjust it as symmetrically as possible, the success in the adjustments being judged from the symmetry of the motion of the particles. The velocity of the stream was adjusted until eddying began. As the velocity is increased further the eddies become larger, their centres become more widely separated and their distances from the obstacle increase. The velocity at which the eddies begin was determined from the time taken to fill a definite portion of the eleven-litre vessel. The temperature of the air stream was observed. Tobacco smoke was used. From five to ten observations of the critical velocity were obtained for each sphere. A very small light-stop had to be used to make the heating effect negligible.

If the dimensions of the channel could be taken as infinite, the physical data determining the critical velocity would be the viscosity,  $\mu$ , and density,  $\rho$ , of the air, and the diameter,  $d$ , of the obstacle. The method of dimensions then leads to Osborne Reynolds' equation

$$v_c = A \frac{\mu}{\rho d},$$

where  $A$  is a constant. In reality, however, the dimensions and form of the channel have some influence. The factor  $A$  is then a numerical function involving the diameter  $D$  of the channel. We shall assume as an approximation that

$$v_c = \frac{\mu}{\rho d} \left\{ A_1 + A_2 \left( \frac{d}{D} \right)^n \right\},$$

where  $A_1$  and  $A_2$  are constants.

All the experimental results at different temperatures were reduced to 20° C., assuming Sutherland's formula as modified by Fischer\* for the temperature coefficient of viscosity.

The above formula was found to fit nearly for different spheres and channels if  $n$  is taken as  $3/2$ . This was tested by plotting  $\frac{v_c d \rho}{\mu}$  against  $\left( \frac{d}{D} \right)^n$ , as shown in fig. 1.

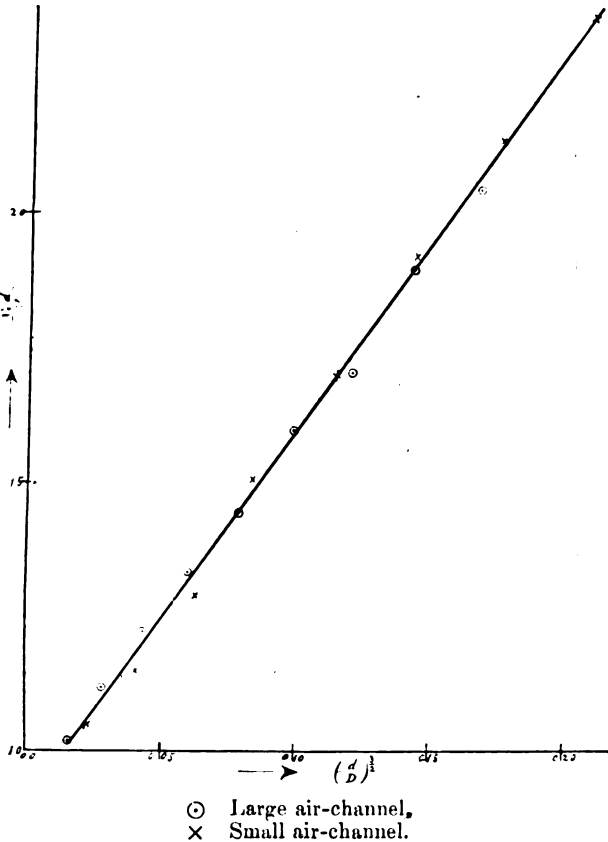
The values of  $A_1$  and  $A_2$  are 8.15 and 68.2 respectively.

Some doubt may be felt in regard to the influence of the supporting needle. This was tested by replacing it in the case of the smallest sphere by a fine hair-spring of a watch

\* Phys. Rev. xxiv. p. 385 (1907).

(0.27 mm.  $\times$  0.07 mm.). No difference was detected that would affect the general slope of the curve.

Fig. 1.—Sphere.



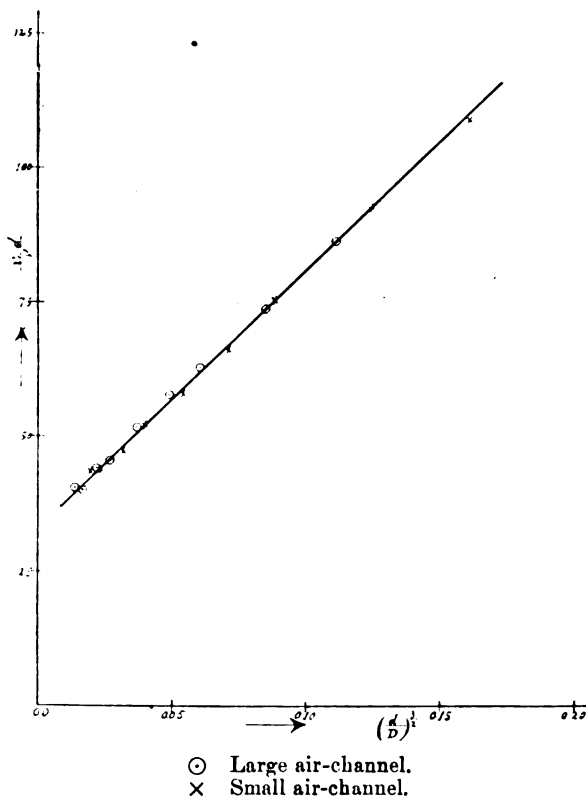
### B. Cylinders.

Nine cylinders of various diameters (1.46 mm. to 5.94 mm.) and 3.2 cm. length were carefully turned on a lathe. A cylinder was supported vertically and symmetrically across the air channel (which was horizontal). The motion was considered as being nearly two-dimensional—at least in the middle of the vessel. The same formula as for a sphere was found to be applicable, as shown in fig. 2; the values of  $A_1$  and  $A_2$  being 2.65 and 48.2 respectively.

It was more difficult to get the two sets of eddies symmetrical in this case. No periodic eddying motion was

observed, such as has been obtained by Kármán and Rubach, Nayler and Frazer, and others. The maximum value of  $\frac{v d \rho}{\mu}$  which we could reach was, however, only 50, and

Fig. 2.—Cylinder.



measurements were difficult before this value was reached. The value at which it was obtained in the case of the last pair of observers was 150.

### C. Plates.

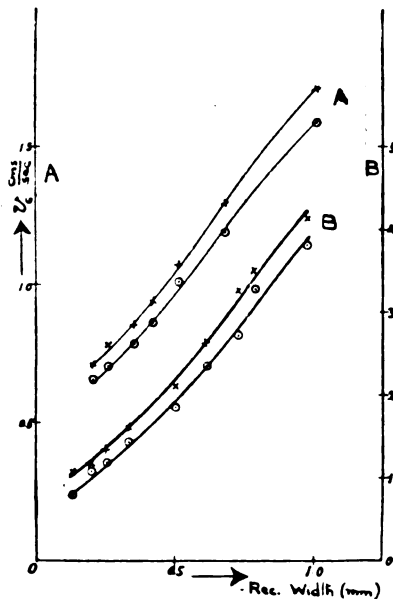
It is clear that the case of plate obstacles is not so simple as the others, because even if they be treated as infinitely long there are both the breadth and the thickness to take into account. Moreover, the indefinite sharpness of the edges introduces additional complication. The usual simple theory which allows infinite velocity at a sharp edge gives us no help.

The experiments were carried out (a) with plates of various widths but of constant thickness; (b) with plates of various thicknesses but constant width; and (c) with plates for which the thickness was in the same ratio to their width. The specimens were made of watch-spring when the thickness was small; in other cases they were brass or zinc plates. In each case the plate was placed with its length perpendicular to the air-current, the final testing being made by an examination of the degree of symmetry of the eddies.

(a) *Plates of constant thickness.*

Two sets were examined. In one set the thickness was 0.15 mm. and in the other 1.62 mm. The range of width in

Fig. 3.—Plates of equal thickness.



- Large air-channel.
- × Small air-channel.
- A Thickness = 0.15 mm.
- B Thickness = 1.62 mm.

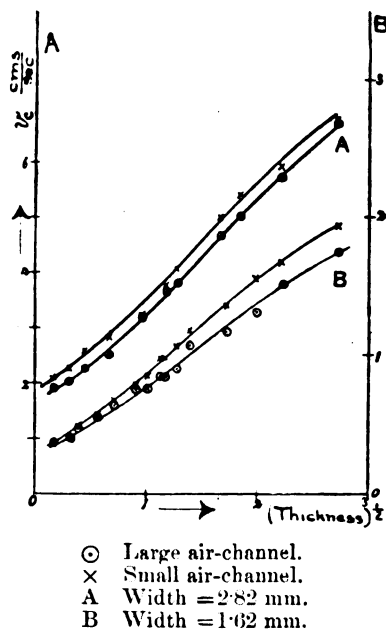
the former set was from 1 mm. to 5 mm.; in the latter set from 1 mm. to 7.5 mm. A small correction was applied by the method of successive approximation on account of small differences in the approximately constant thickness. All the observations were reduced to 20° C. If we plot the critical velocities against the reciprocal of the width, two nearly parallel straight lines are obtained which correspond to the two air-channels, as shown in the curves A and B on fig. 3.

The curve A is for the thinner plate. There is a tendency for the values to become constant when the width decreases, and further, it would seem that the critical velocities do not tend to zero however great the width becomes.

(b) *Plates of the same width.*

Two sets of plates were studied; in one set the width was 1.52 mm., and the thickness varied from 0.03 mm. to 7.5 mm.; in the second set the width was 2.82 mm., and the thickness varied from 0.03 mm. to 9.5 mm. Plotting the critical velocities against the square roots of the thickness, the curves A and B (fig. 4) are obtained for the 2.82 mm.

Fig. 4.—Plates of same width.



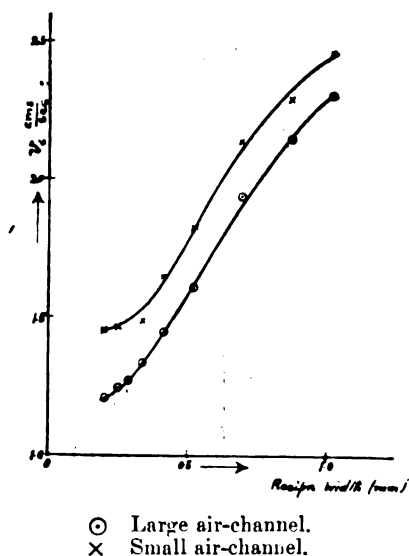
and 1.62 mm. widths respectively. There is a tendency to approach to constant values as the thickness increases. No effects of vibration were observed, although some of the plates were very thin.

(c) *Constant ratio plates.*

The constant ratio of thickness to width was  $1/2$ , while the thickness varied from 0.5 mm. to 2.5 mm. The curves

on fig. 5 represent the critical velocities plotted against the reciprocals of the widths. Simple power laws do not appear to be valid over the whole range, but we may state that the critical velocity changes with the square root of the thickness and the reciprocal of the width as long as the dimensions of the plate are moderate compared with that of the air-channel.

Fig. 5.—Constant ratio plates.



Experiments were also made in a few cases for which the section was not rectangular. A trapezoidal cylinder was taken of which the parallel sides had widths of 2 mm. and 3 mm. respectively. The air-current was incident alternately on the wide and on the narrow side; in the former case the critical velocity was 1.9 times the value for the second case. Again, in the case where the cylinder had a triangular section, when the air flows from the apical line to the corresponding base the critical velocity is about four times larger than in the case of reversed flow.

The following general remarks should be made:—

(1) There was special difficulty in fixing the precise value of the critical velocity, both when the obstacles are very large and very small.

(2) The viscosity and the temperature coefficient for the mixture of air and smoke was taken as being the same as for air.

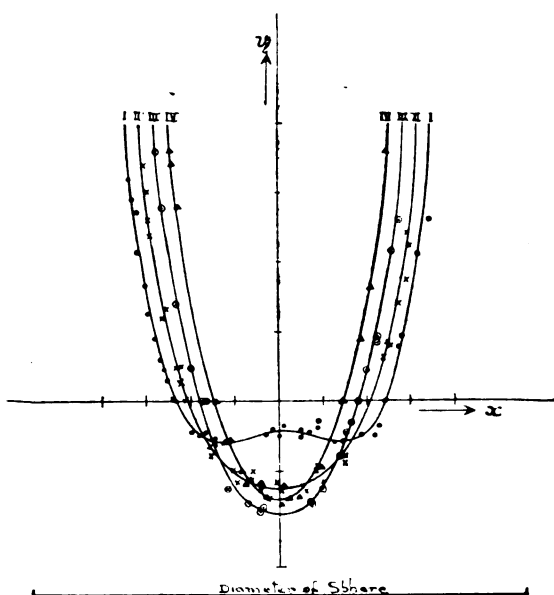
(3) The observation windows in the air-channel would have some effect. The length of the channel is also not without influence, as was shown by making a few determinations with a very short channel. In the actual experiments the channel was long enough for the eddies formed at the inlet to subside. This was tested by taking a photograph without an obstacle—the smoke streaks indicated that the velocity was practically constant and uniform in the neighbourhood of the axis of the channel.

## PART II.

This part of the paper deals with the velocity distribution in the eddies when they are formed.

Several methods have been used to study this distribution. By using a magnesia cloud obtained by burning magnesium ribbon instead of tobacco smoke\* and a full aperture lens,

Fig. 6.—Sphere (longitudinal components).



the field was bright enough to take “instantaneous” photographs of the particles. This was done after suitable steady eddies had been obtained by modifying the velocity

\* Ammonium chloride was also tried, but it settles on the obstacle and on the walls of the channel.

of the current. Each magnesia particle is represented on the photograph by a line whose direction and length represent the direction and magnitude of the velocity in the corresponding region of the eddy. The duration of the exposure was varied from  $\frac{1}{5}$  to  $\frac{1}{20}$  second, depending upon the velocity of the stream. Since a high velocity is needed to produce eddies with small obstacles, the investigation was restricted to the medium-sized obstacles.

In order to measure the photographs obtained, each of them was placed in a lantern in turn and a magnified

Fig. 7.—Sphere (transverse components).

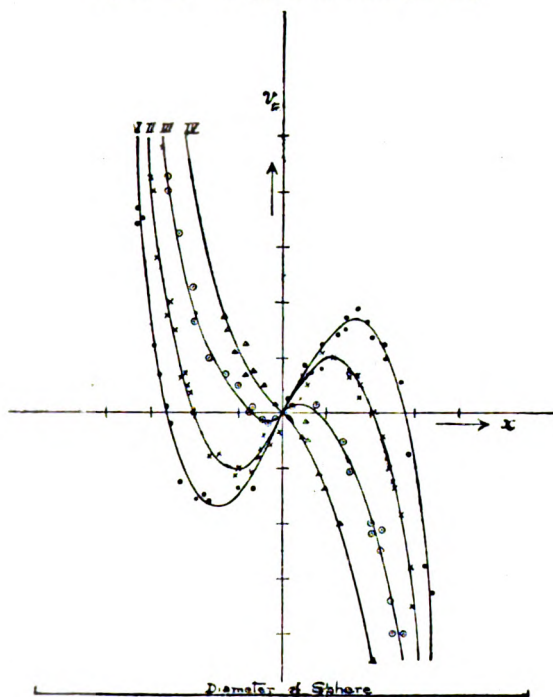


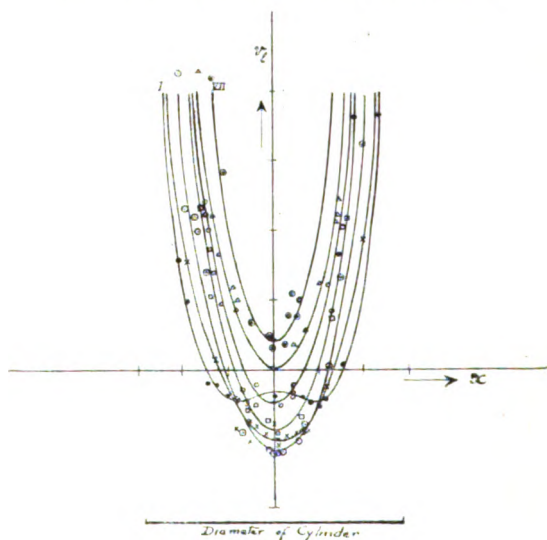
image (about 30 times magnification) was projected upon squared paper. The rectangular components of the streaks were then measured, and thus the longitudinal and transverse velocity components in the eddy were obtained. Each of these components was then plotted (in separate diagrams) against the position in the eddy to which it corresponds, the position of the obstacle, the centres of the eddies, and the neutral point (on the axial line) being used as reference



marks. The curves I, II, III, IV in fig. 6 and fig. 7 represent the longitudinal and transverse components of the velocities corresponding to the sections I, II, III, IV shown in photograph A, reproduced in fig. 8 (Pl. XII.), for the case of a sphere 5.56 mm. diameter, the value of  $\frac{v d \rho}{\mu}$  being 24.2, in

the larger air-channel. The curves represent the longitudinal components and all except I bear a resemblance to curves of the second degree. Curve I has a peculiarity near the axis consequent upon the existence of the "dead space." The values of  $x$  are distances measured from the axial line.

Fig. 9.—Cylinder (longitudinal components).



The curves I to VI in fig. 9 and fig. 10 express the longitudinal and transverse components of velocities in the corresponding sections of the photograph reproduced in fig. 11 (Pl. XII.), for the case of a cylinder of diameter 2.85 mm. in the small air-channel for a value of  $\frac{v d \rho}{\mu} = 11.6$ .

The curves I to VII in fig. 12 and fig. 13 show the distributions of the longitudinal and transverse components of

Fig. 10.—Cylinder (transverse components).

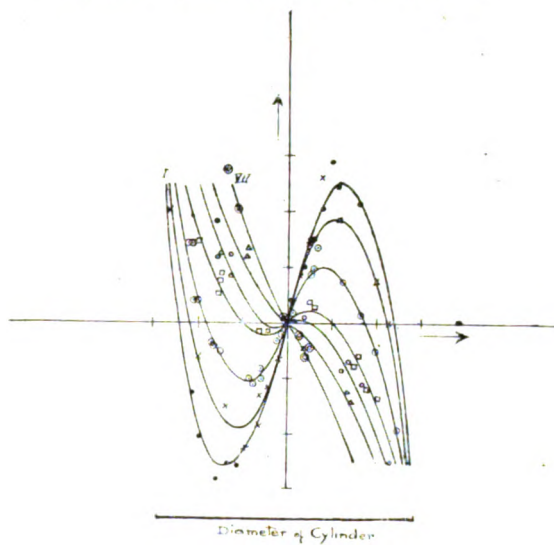
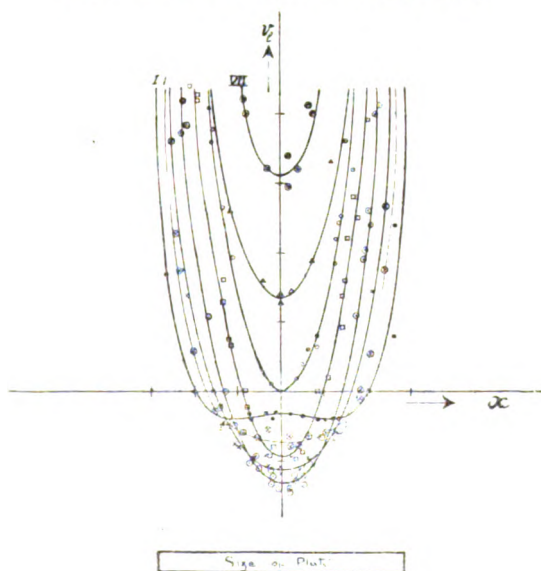
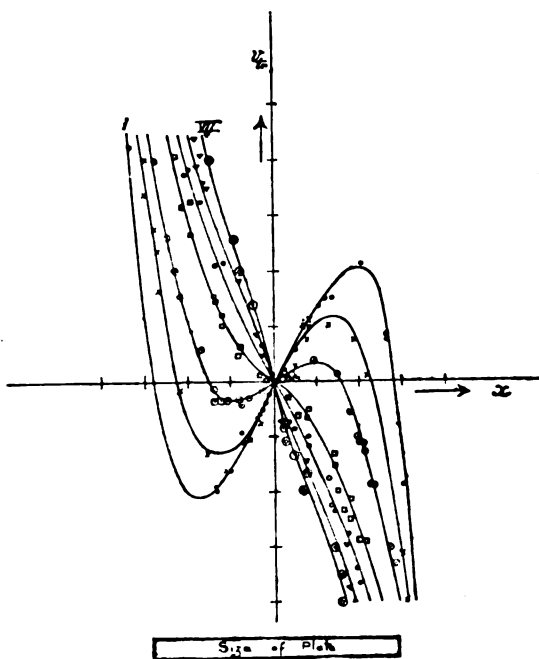


Fig. 12.—Plate (longitudinal components).



velocities in the case of a plate of width 2.82 mm. and thickness 0.21 mm., the value of  $v$  being 1.90 cm./sec. The actual eddies are shown in photograph fig. 14 (Pl. XII). The curve I' corresponds to the section between I and II; it is shown as a fine line on fig. 12, but the section itself is not shown on the photograph. It should be noted that curve V in fig. 13 for the section which passes through the neutral point is nearly a straight line; beyond this section the curvature near the origin probably changes sign.

Fig. 13.—Plate (transverse components).



In fig. 15 (Pl. XII.) is shown another example for a plate-obstacle. In this a longer exposure is given and the general form of the eddy is shown more clearly.

The velocity distribution in front of an obstacle has not been studied in the present investigation. The velocities in that region are great compared with those in the region studied, and difficulties of photography come into play if the streaks are to be kept down to reasonable lengths.

## PART III.

*Relation between the mean velocity and the position of the eddies.*

The photographs of the eddies behind an obstacle were taken for different mean velocities; these images were projected on to squared paper and measured as before.

Fig. 16.

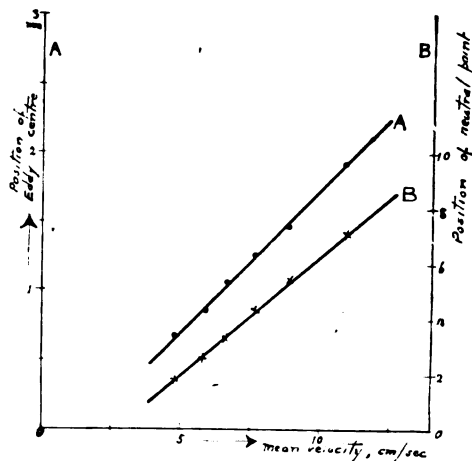
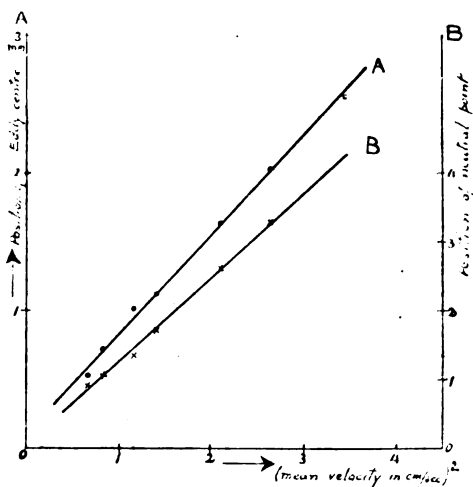


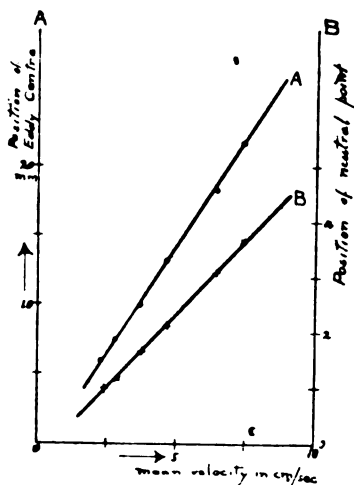
Fig. 17.



Relations are found between the motions of the centres of the eddies and of the neutral point when plotted against the mean velocities, as shown in fig. 16 for a sphere, and on fig. 17,

when plotted against the square of the mean velocity, for a cylinder. The locus of the centres of the eddies is not expressible by the formula which was given by Föppl, but the boundaries were not the same as in his case. The distance of the centres is found to be nearly proportional to the square of the mean velocity.

Fig. 18.



In fig. 18 are shown the corresponding data for a square sectional plate ( $2.8 \times 2.8$  mm.). It was expected that this would approximate to the case of a cylinder. It was found, however, that both for this plate and for a thin plate ( $2.8$  mm.  $\times$   $0.2$  mm.) the distances are proportional to the mean velocity itself.

LXXXVII. *The Distribution of Velocities among the Electrons emitted by Hot Platinum in an Atmosphere of Hydrogen.*  
By HAROLD H. POTTER\*.

Part I.—CONSIDERATIONS OF A GENERAL CHARACTER.

*Introduction.*

THE first measurements on the energy distribution among the electrons emitted by hot metals were made by Prof. O. W. Richardson and F. C. Brown†, and by O. W. Richardson‡. Both the normal and the tangential components

\* Communicated by Prof. O. W. Richardson, F.R.S.

† Phil. Mag. xvi. p. 353 (1908).

‡ Phil. Mag. xvi. p. 890 (1908); xviii. p. 681 (1909).

of the velocity were studied, and the experiments showed that the distribution of energy among the electrons emitted by platinum in air at low pressures was in close agreement with Maxwell's Distribution Law for a gas of molecular weight equal to that of the electrons in thermal equilibrium at the temperature of the hot platinum. Some experiments were also made on lime-coated filaments and on platinum filaments in an atmosphere of hydrogen. In both cases the velocity distribution did not appear to be in agreement with Maxwell's law. The experiments on lime-coated filaments seemed to give fairly definite results, but in the case of hydrogen—to quote the authors—"the results were too irregular to draw very definite conclusions from." The present series of experiments were undertaken in the hope of clearing up some of these points.

The experiments of Richardson and Brown were carried out with plane parallel electrodes. Schottky \*, later, measured the velocity distribution among the electrons emitted by carbon and tungsten filaments surrounded by cylindrical electrodes. Schottky found that although the linear relation between the logarithm of the current and the retarding voltage held good, the average energy of the electrons was greater than demanded by theory.

In 1917 further experiments on platinum and tungsten were made in this laboratory by Mr. Sih Ling Ting †, using the cylindrical anode method, and the results appeared to confirm the view that the average energy was greater than that demanded by Maxwell's law. The whole question has been recently re-examined at the instigation of Prof. Richardson by J. H. Jones ‡, who has shown that in the case of tungsten, Maxwell's law is satisfied both as regards the linear relation between the logarithm of the current and the voltage and as regards the value of the average energy. The high energy values of Ting have been shown to be due to faulty circuit arrangements. Similar conclusions have recently been reached by L. H. Germer § and in the present paper. There is no longer any doubt but that the electrons emitted from a clean metal surface *in vacuo* possess a Maxwell velocity distribution.

\* *Ann. d. Phys.* xliv. p. 1011 (1914).

† *Proc. Roy. Soc. A*, xcvi. (1921).

‡ *Proc. Roy. Soc. A*, cii. p. 734 (1923).

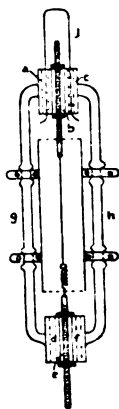
§ *Science*, lvii. p. 392 (1923).

*Description of Apparatus.*

The apparatus and electrical connexions were practically the same as the second arrangement used by Dr. Jones in his investigation of the energy distribution of the electrons emitted by hot tungsten (Jones, *loc. cit.* fig. 8, p. 744).

The construction and the mountings of the thermionic tube are shown in figs. 1 and 2. The cylinder and the filament were mounted on a quartz frame, as shown in fig. 1. *a, b, c, d, e, f* are six pieces of quartz capillary tubing 16 mm. long and 1.5 mm. internal diameter, made together in groups of three and fixed by quartz rods *g* and *h* so that the tubes *a, b, c* are directly opposite the tubes *d, e, f*. The filament was secured at one end to a copper rod and at the other end to a molybdenum spring, which in its turn was fastened to a second copper rod. The copper rods were threaded, and held in position in the tubes *b* and *e* by four small nuts. The cylinder was secured to the quartz frame by riveted copper bands, as shown. *j* is a hook, used to support the quartz frame inside the exhausted tube.

Fig. 1.



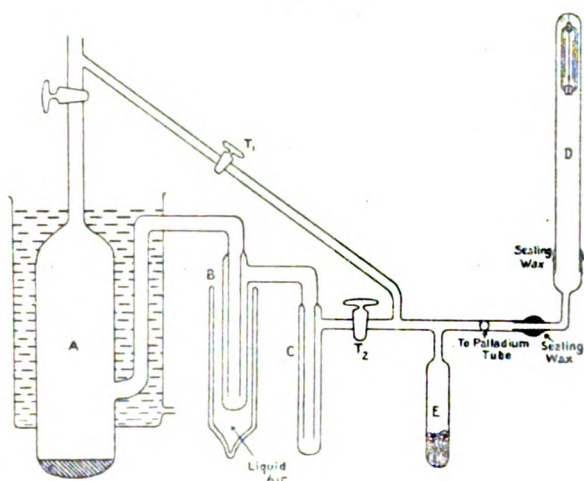
This quartz frame, which had been used previously by Dr. Jones for other work, was admirably suited for use in this experiment. One of the principal points in mind in designing the apparatus was to obtain an arrangement in which the filament could be replaced easily. The high volatility of platinum makes it well-nigh impossible to work with any one filament for a long period, and consequently it was important to be able to replace filaments easily and quickly. This condition is evidently fulfilled by the quartz frame arrangement, the removal of the filament being merely a matter of unscrewing a few nuts. The containing quartz tube was also designed with the same object in view. It consisted of a tube 33 cm. long and 4 cm. internal diameter, fitted with a cap with suitable outlets for electric leads and exhaust. The cap was fixed with sealing-wax, and the exits for the electric leads were also secured with sealing-wax. The tube was fixed in a vertical position with the cap at the lower end. In the upper end of the tube was a quartz hook which served to support the quartz frame, etc.

*Pumps, etc.*

The exhausting of the tube was carried out by means of a mercury vapour diffusion pump backed by a Gaede and an oil pump.

The connexions between the diffusion pump A and the tube are shown in fig. 2. The diffusion pump A was connected through two liquid-air traps B and C (used to keep the mercury vapour out of the quartz tube) to the quartz tube D. E is a charcoal tube which can be surrounded by liquid air. A tube was provided to short-circuit the diffusion

Fig. 2.



pump so that air could be let into the quartz tube and subsequently pumped out without admitting air to the diffusion pump. When the diffusion pump was being used the tap  $T_1$  was of course closed. Hydrogen could be admitted to the apparatus by means of a palladium tube.

*Cleaning up of Quartz Tube and Electrodes.*

The object of using quartz apparatus was to facilitate the cleaning-up process. With glass it is extremely difficult to get rid of the occluded gases, and it is impossible without the aid of a vacuum furnace to raise a glass tube to a sufficiently high temperature to clean up the metal inside. In these experiments the tube was heated by means of an electric furnace at a temperature of about  $1000^{\circ}\text{C}$ .



for two or three hours, a vacuum being maintained meanwhile by the working of the mercury vapour pump. The rapid evolution of gas by the various parts of the apparatus at these high temperatures made it impossible to maintain a high vacuum, but the mercury diffusion pump was so rapid in its working that the pressure after the first few minutes' heating rarely rose above 1000 mm. of mercury. The speed of the pump is of some importance in another respect. It is well known that at high temperatures quartz is permeable to hydrogen. At the high temperature of the electric furnace the dissociation of water vapour is sufficiently high for hydrogen to have been present in appreciable quantities outside the quartz tube, but any, however, which found its way through the quartz would have been removed too quickly to exert any "permanent" effect on the platinum filament.

With the method of cleaning up described the copier becomes very bright and clean.

This intense heating made it necessary to use a long tube, so that all sealing-wax joints were a long way from the furnace. Heat reached the sealing-wax chiefly by radiation through the evacuated tube and by conduction along the electrical leads. It was found impossible, using a tube 16 cm. long, to keep the sealing-wax hard even with water cooling, but with the long tube described above the joints could be kept quite hard with the help of occasional blasts of cold air.

After heating in the furnace, the tube was allowed to cool gradually, the filament being glowed during the cooling at about 1500° C. This caused a temporary emission of gas by the filament, and at the same time prevented condensation on the filament of any vapours present in the tube.

## Part II.—EXPERIMENTS ON THE VELOCITY DISTRIBUTION.

### *Theoretical Considerations.*

Assuming that the distribution of velocities among the emitted electrons is in accordance with Maxwell's law, the current  $i$  flowing between two parallel plates under a potential difference  $V$  is given by

$$i = i_0 e^{-\frac{Ve}{kT}}, \quad \dots \dots \dots (1)$$

$$\text{or} \quad \log \frac{i}{i_0} = -\frac{Ve}{kT},$$

where  $i_0$  is the saturation current,  $k$  Boltzmann's constant,

T the absolute temperature of the emitting electrode, and  $\epsilon$  the electronic charge. The average kinetic energy of the stream of electrons is  $2kT$ .

Schottky has shown that for cylindrical electrodes the expression is

$$\iota = \iota_0 \sqrt{\frac{2}{\pi}} \left\{ x e^{-x^2} + \int_x^\infty e^{-x^2} dx \right\}, \quad \dots \quad (2)$$

where  $x = \sqrt{\frac{V\epsilon}{kT}}$ , provided the radius of the anode is sufficiently large in comparison with the radius of the wire.

Plotting  $V$  against  $\log_{10} \frac{\iota}{\iota_0}$ , we get, according to equation (1), a straight line given by the equation  $\log_{10} \frac{\iota}{\iota_0} = -\cdot4343x^2$ . Except near  $x=0$ , equation (2) gives a straight-line relation given by  $\log_{10} \frac{\iota}{\iota_0} = -\cdot405x^2$ ,

$$\text{or} \quad \log_{10} \frac{\iota}{\iota_0} = -\cdot405 \frac{V\epsilon}{kT} = -\cdot405 \frac{V\nu\epsilon}{RT},$$

where  $\nu$  = number of molecules in 1 c.c. of a perfect gas at  $0^\circ \text{C}$ . and 760 mm. pressure, and  $R$  is the constant in the equation  $p\nu = RT$  calculated for the stated quantity of gas.

The difference in equations (1) and (2) has been shown graphically by Schottky \* and Ting † :

$$\nu\epsilon = -\cdot4327 \text{ e.m. units,}$$

$$R = 3\cdot711 \text{ ergs/degs. centigrade.}$$

Thus, if  $V$  is in volts,

$$\log_{10} \frac{\iota}{\iota_0} = \frac{4720V}{T}.$$

Thus the slope of the  $(\log \frac{\iota}{\iota_0}, V)$  curve is inversely proportional to the temperature and to the average energy of the electron stream. One obviously arrives at the same value of the slope by plotting  $\log \iota$  against  $V$ . Further, the units in which  $\iota$  is measured do not affect the slope. In the results given in the graphs below,  $\iota$  has been given in terms of the galvanometer deflexion.

\* *Ann. d. Phys.* xliv. p. 1018 (1914).

† *Proc. Roy. Soc. A*, xcvi. p. 378.

Owing also to the presence in the tube of a contact potential, it was difficult to tell the exact value of the retarding or accelerating voltage; but this does not constitute a real difficulty, as it is only necessary, in order to obtain the slope of the  $(\log i, V)$  curves, to note the change in the current produced by a given increment in the voltage. The voltage shown in the graphs is that registered by the voltmeter.

#### *Method of Experimenting.*

The main object of this part of the work was to obtain a clean platinum filament which had not been heated in hydrogen, to measure the slope of the  $(\log i, V)$  curve at a definite temperature, and then to admit hydrogen to the apparatus and again measure the slope at the same temperature.

#### *Temperature of Filament.*

An accurate knowledge of the actual temperature of the filament was not necessary in these experiments, but a rough estimate from pyrometric and resistance measurements gave about  $1450^{\circ}\text{C.}$  as the temperature at which nearly all these experiments were made. It was found advisable not to go much above this temperature, as the volatility of the platinum was so high that the filaments soon fused.

In order to keep the filaments at a constant temperature, the resistance was kept at a constant multiple of the resistance at room temperature. This was the method used by H. A. Wilson to keep the temperature of the filament the same in high vacuum and in hydrogen.

#### *Phenomena connected with cleaning up of Filament.*

Various methods of cleaning up the filament have been used by other experimenters. H. A. Wilson in his work used nitric acid, but this may contaminate the surface with an oxide. Lockrow suggests alternate heating of the filament in hydrogen and oxygen. The writer has found this method very successful, but on the other hand it does not seem desirable in experiments designed to show the effect of hydrogen on the emission from platinum to first of all clean up the platinum by heating it in hydrogen. The method adopted in this experiment was to clean up the wire entirely by heating in high vacuum at a high temperature. Herein lay the greatest difficulty of the experiment. The melting-point of platinum is low and its volatility high, so that it was

difficult to remove the more refractory impurities. In fact, a large proportion of the filaments fused before the impurities had been driven off. However, by the exercise of a sufficient amount of patience, a considerable number of filaments have been found to give satisfactory results.

After the heating in the furnace and the driving of gas from the filament described above, a high vacuum was produced by the diffusion pump, and then the taps  $T_1$   $T_2$  (fig. 2) were closed and liquid air applied to the charcoal tube. In general the electron emission was at first very small, but after a few hours' glowing of the filament it began to grow. On the other hand, the initial currents were sometimes abnormally high—due perhaps to the presence on the wire of substances such as lime, which have a high electron emissivity. Occasionally the cleaning-up process was complete in about three hours, but usually took anything up to twenty-four hours, and sometimes as much as sixty hours.

The best criteria of the wire being clean appear to be the stability of the emission and the shapes of the current potential curves. If the filament is clean the emission readily saturates, but if it is dirty it is very difficult to get saturation, owing probably to the existence of local fields at the surface of the wire.

### *Results.*

In all experiments which have been made, the linear relation between the logarithm of the current and the voltage has been found to hold good at low values of the current. For higher values of the voltage, the current was found to increase less rapidly with the voltage than would satisfy a linear relation. This is exactly as demanded by theory.

*Experiment 1.*—Tube heated  $2\frac{1}{2}$  hours in furnace, and filament subsequently heated for 3 hours in high vacuum.

Four curves similar to fig. 3, showing current potential relations in high vacuum, gave slopes of the log curves equal to 2.70, 2.53, 2.90, and 2.60. Mean = 2.68.

*Experiment 2.*—No heating of tube in furnace, as copper anode and tube were already very clean. Filament glowed 24 hours in high vacuum.

Measurements were made in hydrogen at a pressure of 0.25 mm. Three curves similar to fig. 4 gave slopes of the log curves equal to 2.05 and 1.95 respectively. The slope of the log curve for emission *in vacuo* was 2.5.

Fig. 3.

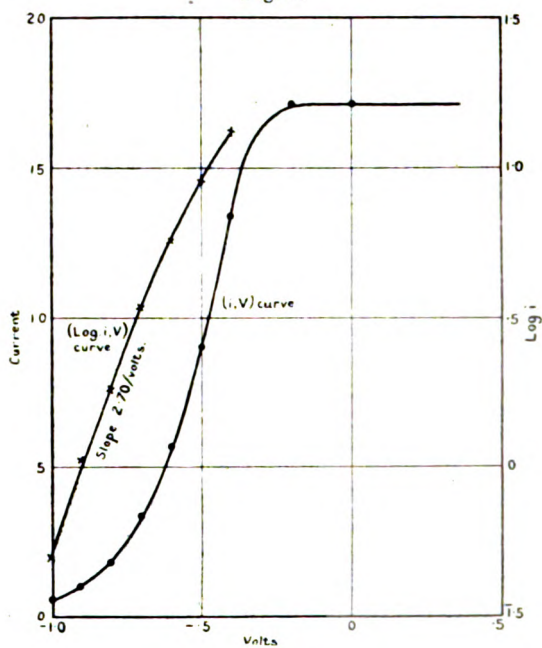
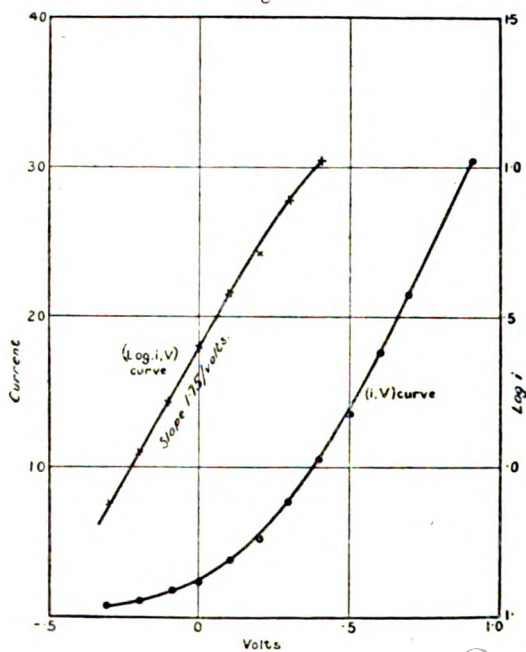


Fig. 4.



*Experiment 3.*—Tube heated in electric furnace for 2 hours, and filament subsequently heated in high vacuum for 2 hours.

Three curves showing current voltage relations were obtained. Two gave slopes of 2.65 and 2.75 in high vacuum; the other was obtained with a pressure of hydrogen =  $\frac{185}{1000}$  mm. and gave a slope = 1.75.

*Experiment 4.*—Two hours' heating in electric furnace followed by alternate heating of filament in hydrogen and air.

The results of this group of experiments in the order in which they were made are as follows:—

Slope of log curve.	Pressure of Hydrogen (mm. $\times 10^{-3}$ ).
2.78	0
2.60	0
2.82	0
2.52	15
2.60	40
1.75	175
1.75	70
1.61	54
2.55	22
1.90	140
2.90	0
1.50	145
2.75	0
2.40	400

*Experiment 5.*—Tube heated 2 hours in furnace, and filament subsequently glowed alternately in hydrogen and high vacuum.

Two curves were obtained, showing a slope of 2.46 for curve obtained *in vacuo* and 1.31 in hydrogen at .30 mm.

### *Discussion of Results.*

The five series of results given above show clearly that for pressures of hydrogen greater than  $\frac{50}{1000}$  mm. the slope of the (log  $\iota$ , V) curve is less than in vacuum.

A mean of thirteen experiments in high vacuum gave 2.68 volts as the slope of the (log  $\iota$ , V) curves. The slope demanded by theory, if Maxwell's law is obeyed, is 2.72 at a temperature of 1450° C.

In the presence of hydrogen the linear relation between log  $\iota$  and V has been found to hold, but the slopes of the various curves have very low values. The mean of thirteen measured values of the slope at various pressures of hydrogen is 1.96. The writer has been unable to find any relation

between the pressure of the gas and the slope of the curve. Slopes as high as 2.40 have been measured at a pressure of  $\frac{400}{1000}$  mm. of hydrogen, and as low as 1.31 at  $\frac{300}{1000}$  mm. and 1.61 at  $\frac{51}{1000}$  mm. The previous treatment of the wire is undoubtedly of importance, and the effect is of a semi-permanent nature. With increasing pressures of hydrogen the slope does not at first appear to decrease very much, but if a low slope has once been obtained and the gas is then pumped out, the slope remains low until a fairly small pressure has been obtained, when it will suddenly increase. This is shown in readings 1 to 9, Experiment 4.

The effect is undoubtedly of a complicated nature, and in the absence of further evidence it is impossible to say exactly on what conditions the low slope depends. The one fact, however, remains that with five different specimens of platinum the slope of the  $(\log i, V)$  curves has without a single exception been found to be abnormally low for pressures of hydrogen above  $\frac{1}{20}$  mm. These low slopes may arise in two ways:

1. Through the agency of local fields at the surface of the filament.

2. By an actual increase in the energy of the electrons.

The writer has measured the slope of the  $(\log i, V)$  curves for a tungsten filament, sputtered with thorium, in which these local fields are supposed to exist. It has been found that the slope of these curves is considerably below that required by Maxwell's law.

One of the requirements of the local field theory, however, is apparently that the current-potential curves should not easily saturate. This is known to be so in the case of thorium-sputtered filaments, but the writer has found no evidence to support this explanation of the low slopes of the curves from platinum. Fig. 5 shows one of these low-slope curves, and fig. 6 shows the same curve on a different scale for potentials up to 8 volts. The saturation is seen to be almost perfect and to be complete at zero voltage.

The low slopes cannot be occasioned by the shortness of the mean free path, as there seems to be no theoretical reason why elastic collisions should affect the energy distribution. Further, F. C. Brown\* has shown that the energy distribution amongst the positive ions emitted from platinum is independent of the gas- (air) pressure from

\* Phil. Mag. xvii. p. 355 (1909).

·009 mm. to 28·0 mm.—a very much greater range than has been used in the writer's experiments. Also any effect due to collisions would be expected to be some regular function of the gas-pressure. We are led, therefore, to conclude that the average energy of the electrons emitted from platinum, as measured by this method, is higher in an atmosphere of hydrogen than in vacuum. Exactly how this may be brought about is not readily explained. Prof. Richardson has made

Fig. 5.

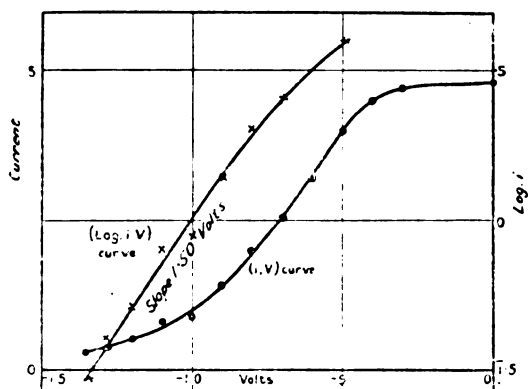
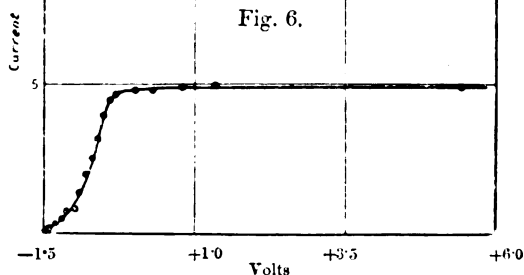


Fig. 6.



two suggestions—(1) that owing to the presence of the hydrogen the surface of the wire is in a state of polarization, and that the electrons are consequently emitted with a velocity above the normal ; (2) that the electrons may start with a Maxwell distribution which is subsequently modified by local fields of force, thus giving rise to the abnormal measured values. This seems to be excluded if easy saturation can be considered as a reliable test for the absence of local fields. We cannot, however, be sure that it is.



780 Mr. H. H. Potter on *Distribution of Velocities among*  
 Part III.—SOME EXPERIMENTS ON THE EFFECT OF HYDROGEN  
 ON THE TOTAL EMISSION FROM PLATINUM.

In 1904, H. A. Wilson \* came to the conclusion that the emission of electrons from hot platinum was greatly increased in the presence of hydrogen. This became the subject of a number of researches by O. W. Richardson †, F. Horton ‡, G. H. Martyn §, Lockrow ||, among others.

The results of these researches were of a complicated nature, but the main points were as follows:—

With “new” wires (*i.e.*, wires which have not been subjected to prolonged heating in hydrogen) the emission at a given temperature was increased on admitting hydrogen to the apparatus. “Old” wires were found to give an emission independent of the pressure of hydrogen.

In view of the effect of hydrogen on the average energy, it is interesting to examine the effect on the total emission under the same conditions. The experiments described in this section were carried out with the same filaments and at the same time as the experiments on the velocity distribution described above.

*Results.*

In the results given below, the values of the saturation currents from five different samples of platinum are given for vacuum and for various pressures of hydrogen. The currents are given in terms of galvanometer scale deflexions. The sensitivity of the galvanometer was 1 cm. deflexion for  $3 \times 10^{-9}$  amp. The thermionic circuit was “made” for about  $\frac{3}{8}$  of the total time, so that 1 cm. deflexion represented a current of  $8 \times 10^{-9}$  amp. The diameter of the filaments was .05 mm. and the length about 3.5 cm., so that a deflexion of 1 cm. represented a current density of  $7 \times 10^{-8}$  amp. per sq. cm.

*1st Experiment.*—Same wire as Experiment 1, Part II.

Tube heated  $2\frac{1}{2}$  hours in furnace, and filament subsequently heated for 3 hours in high vacuum.

Sat. current (cm. scale divisions).	Pressure of hydrogen (mm. $\times 10^{-3}$ ).
17.10	0
18.00	0
13.70	0
14.10	0
12.00	200
13.00	0
18.60	0

\* Phil. Trans. A, ccii. p. 243 (1904); Phil. Trans. A, ccviii. p. 247 (1908); Proc. Roy. Soc. A, lxxxii. p. 71 (1909).

† Phil. Trans. A, ccvii. p. 1 (1906).

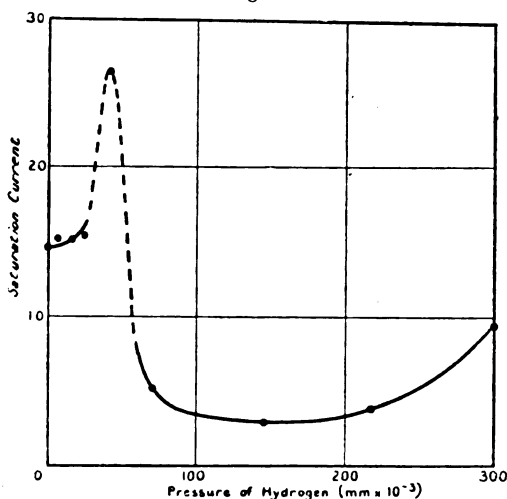
‡ Phil. Trans. A, ccvii. p. 149 (1908).

§ Phil. Mag. (6) xiv. p. 306 (1907). || Phys. Rev. p. 97, Feb. 1922.

After further prolonged heating of filament in high vacuum :—

Sat. current (cm. scale divisions).	Pressure of hydrogen (mm. $\times 10^{-3}$ ).
8.00	0
10.80	250
9.80	150
10.00	90
9.80	50

Fig. 7.



After this series of figures was taken, some air was let into the apparatus. The emission fell off at once to something too small to be measured with the galvanometer. Pumping out the air and admitting hydrogen immediately restored the emission to its former value.

*2nd Experiment.*—Same filament as in Experiment 2, Part II.

No heating in furnace as copper anode and tube were clean. Filament glowed about 24 hours in high vacuum.

Saturation current (cm. scale divisions).	Pressure of hydrogen (mm. $\times 10^{-3}$ ).
13.70	250
10.15	0
11.75	250
11.75	0

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3rd *Experiment*.—Same filament as in Experiment 3, Part II.

Two hours' heating in electric furnace and 2 hours' glowing of filament in high vacuum.

Saturation current (cm. scale divisions).	Pressure of hydrogen (mm. $\times 10^{-3}$ ).
33.70	0
35.00	350
36.4	0
25.8	175
53.0 (f)	165

4th *Experiment*.— $1\frac{1}{2}$  hours' heating in furnace. Filament glowed for 60 hours in high vacuum.

Saturation current (cm. scale divisions).	Pressure of hydrogen (mm. $\times 10^{-3}$ ).
15.05	0
16.00	260
13.00	8
9.00	125

5th *Experiment*.—Same filament as in Experiment 4, Part II.

Two hours' heating in electric furnace followed by alternate heating of filament in hydrogen and air.

Saturation current (cm. scale divisions).	Pressure of hydrogen (mm. $\times 10^{-3}$ ).
9.35	0
7.80	100
7.80	0
7.30	0
20.50	15
27.10	40
10.30	175
6.50	70
5.60	54
19.50	22
6.80	140
16.90	0
10.50	0
5.25	145
12.60	0
14.55	0
14.60	400
17.90	0

*Discussion of Results.*

The five sets of results tabulated above were obtained with five different specimens of platinum. In each of the first four groups the wire was cleaned by heating for a prolonged period in high vacuum. There was little or no indication of any increase in the emission from the filament when hydrogen was introduced into the tube. The one case where an appreciable increase was noticed (the last reading of Experiment 3) may be explained as follows:—The filament

fused soon after this reading was taken, which means that one part of the wire had got very hot, and so was emitting strongly. It is quite likely for this to happen in spite of the total resistance of the wire being kept constant by control of the heating current. Apart from this one instance, there are no changes in the emission which could not be attributed to changes of temperature.

The fifth group of experiments in which the wire was cleaned by alternate heating in hydrogen and oxygen gave results of a somewhat different nature. The inference from this series of results would be that for pressures of hydrogen below  $\frac{1}{20}$  mm. the emission was somewhat greater than in a vacuum, but for the pressures above this value it was less. This set of readings does not, however, appear to be as reliable as the four preceding sets, the vacuum currents varying from 5.25 cm. to 17.90 cm.

*Some Peculiar Phenomena observed during the above Experiments.*

Two distinct kinds of phenomena have been observed under what appeared to be identical conditions.

1. A platinum filament which had been thoroughly cleaned by prolonged heating in high vacuum was found to give exactly the same emission after admitting hydrogen as it gave in high vacuum. On pumping out the hydrogen, however, the emission gradually decreased in a manner which made it roughly proportional to the pressure of the gas. At a pressure of  $\frac{1}{10,000}$  mm. (the limit of the Gaede pump) the emission was practically zero. It could, however, be restored (*a*) immediately by admitting hydrogen, (*b*) gradually by applying liquid air to the charcoal tube and glowing the filament at about 1450° C. The phenomenon occurred with two different wires, and could be repeated almost indefinitely with either wire.

2. A phenomenon of somewhat different type was observed with other wires. Up to a point the phenomenon was the same as that described above, but on pumping out the hydrogen the emission decreased less quickly, and at a certain value of the pressure—always between  $\frac{1}{20}$  mm. and  $\frac{1}{100}$  mm.—the emission suddenly increased to about twice the vacuum value. With further reduction in the pressure the emission fell off steadily to the vacuum value. With increasing pressures of hydrogen the emission was not similarly affected. Further, if when the high emission was obtained the taps were closed so as to keep the pressure constant, the emission fell off gradually to the vacuum value.

These are only two of a large number of peculiar results obtained with platinum filaments in hydrogen, but these two have been mentioned because they have occurred so many times and with various samples of platinum.

The first peculiarity may be merely the result of a little air entering the tube when the taps were opened to start pumping out, but the effect was persistent even when the apparatus had been washed through several times with hydrogen. In the absence of further information, it is difficult to give any adequate explanation of the second effect mentioned. The effect is shown in fig. 7.

*Relation between Average Energy and Total Emission.*

There appears to be no relation between the measured average energy and the total emission from the filament; the energy was always increased on admitting hydrogen, whereas the effect on the total emission was quite small, any existing variation being sometimes in the direction of increasing current and sometimes in the reverse direction.

SUMMARY.

The electron emission from hot platinum has been measured in vacuum and in an atmosphere of hydrogen. The presence of hydrogen at pressures of  $\frac{1}{10}$  mm. and over has been found to greatly affect the measured average energy of the emitted electrons.

Maxwell's Distribution Law has been found to hold for the emission from pure platinum in a high vacuum. The linear relation between the logarithm of the current and the applied voltage has been found to hold good in an atmosphere of hydrogen, but the average energy of the electrons has been found to be higher than that demanded by Maxwell's law. The average energy does not appear to be a regular function of the pressure.

Experiments on the total emission have indicated that if the platinum wire is quite clean hydrogen has little or no effect on the total emission at temperatures near  $1450^{\circ}\text{C.}$ , but that the hydrogen has a considerable effect (usually increasing the emission) if the filament is contaminated (*cf.* Lockrow, *Phys. Rev.* p. 97, Feb. 1922).

I wish in conclusion to express my gratitude to Prof. Richardson for initiating these experiments, and for many valuable suggestions in carrying them out.

Physics Research Laboratories,  
King's College, Strand.  
October 1922.

LXXXVIII. *The Entrainment of Air by a Jet of Gas issuing from a Small Orifice in a Thin Plate.* By J. S. G. THOMAS, D.Sc. (Lond. and Wales), A.R.C.Sc., A.I.C., Senior Physicist, and E. V. EVANS, F.I.C., Chief Chemist, South Metropolitan Gas Company\*.

*Introduction.*

IN a previous communication†, one of us has discussed the discharge of air at atmospheric temperature through a small orifice in a thin plate, and the entrainment of air by the jet of issuing gas. In the paper referred to the effects of size of orifice and of pressure at the orifice upon the discharge and air entrainment were more especially investigated. Recent developments within the gas industry, since the passing of the Gas Regulation Act, 1920, which conferred freedom upon individual gas undertakings to supply gas of any declared calorific value, have made a knowledge of the dependence of the air-entraining power of a gas jet upon various other factors extremely desirable. The efficient operation of any gas-burner of the Bunsen type depends primarily upon efficient air induction by the jet of gas issuing from the ejector of the burner. Towns' gas consists of a mixture of certain combustible constituents, viz., hydrogen, methane, ethane, carbon monoxide, and various unsaturated hydrocarbons, together with certain incombustible gases generally classified together as "inerts" and including nitrogen, oxygen, and carbon dioxide. The individual combustible constituents require various respective proportions of oxygen for their complete combustion. Thus while for this purpose hydrogen and carbon monoxide require only half their respective volumes of oxygen, methane requires twice and benzene vapour 7·5 times its volume of oxygen for complete combustion. The incombustible constituents generally are characterized by relatively high specific gravities compared with the combustibles, and it might, we think, be reasonably anticipated that, on this account, the degree of primary aeration of a jet of coal gas effected at any pressure would, *ceteris paribus*, be increased by an increase in the proportion of these "inert" incombustible constituents present in the gas. Under these conditions the designation "inert" would be a misnomer. Various other important practical considerations in connexion with

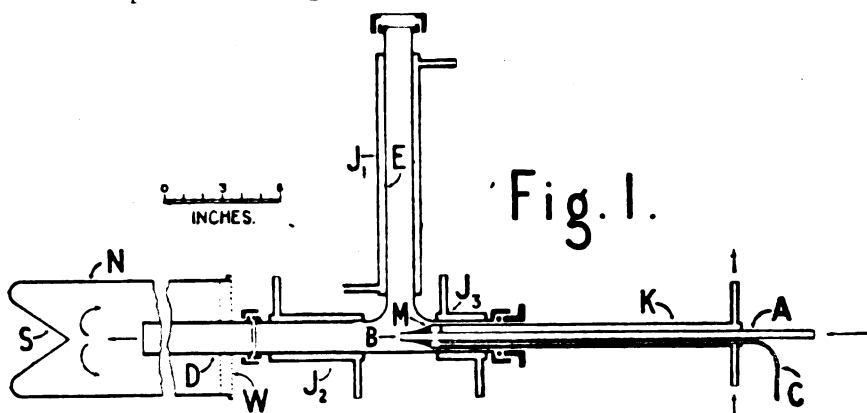
\* Communicated by the Authors.

† Phil. Mag. vol. xlv. p. 969 (1922).

the subject have been summarized in the Ninth Report of the Joint Research Sub-Committee of the University of Leeds and the Institution of Gas Engineers to the latter body (1923). The subject of air entrainment in burners for use with varieties of towns' gas, of calorific values ranging from 3000 B.Th.U. to 600 B.Th.U. per cubic foot and of different specific gravities, has been discussed in recent papers issued by the Bureau of Standards, Washington\*. We propose in the present paper to consider the dependence of air entrainment by a jet of gas upon the density of the gas in the jet and upon the density of the air into which the jet issues. Our experiments are confined to the gases, hydrogen, coal gas, air, and carbon dioxide.

### *Experimental.*

The method of experiment corresponded very closely with that detailed in the previous communication†. In the present work, gases respectively lighter, heavier, and



of the same density as air were employed, and in order to eliminate as completely as possible any effect upon air entrainment arising from a vertical column of gas lighter or heavier than air, the discharge and air induction tubes were mounted horizontally. They are shown in plan in fig. 1 and differ slightly from those used in the previous work. The discharge tube A was provided with a jacket K, through which water, steam, or other heating fluid could be

\* Technologic Papers, No. 193 (1921) and 222 (1922), U.S. Bureau of Standards, Washington.

† Phil. Mag. *loc. cit.* p. 973.

passed. The remaining tubes in the neighbourhood of the orifice B and for some distance therefrom were similarly provided with jackets,  $J_1$ ,  $J_2$ , and  $J_3$ , and the whole of the apparatus comprising the discharge and induction tubes carefully lagged with cotton wool and felt. The jacket  $J_1$  was built in two sections each 15 inches long as shown. The orifice in the disk B was of such diameter that anomalous air entrainment such as that referred to in the previous work \* did not occur within the range of pressures employed. The disk and orifice were carefully prepared from a nickel-steel sheet as previously detailed, and the disk was soldered to the discharge tube by means of hard solder. Pressure in the discharge tube at a point about 1.5 inches from the orifice was transmitted to a water manometer through a chamber M brazed to the discharge tube and connected with the tube C as shown. The pressure was read by a microscope to within 0.02 mm. Air supplied to the discharge tube was dried by passage over calcium chloride. A hot wire anemometer was inserted in the air induction tube E as previously described, to measure the volume of air entrained by the jet, and was arranged in such position that its indication was not affected by the temperature in the jacket  $J_1$ . The mixture of gas discharged from the orifice and air induced by the jet was delivered into a comparatively large cylindrical vessel N provided with a re-entrant conical bottom as shown at S. The effect of external atmospheric disturbances on the jet was reduced to a minimum by providing the mouth of N with two layers of fine copper gauze W.

In the first series of experiments, dry air at a temperature of  $14^\circ \text{C. } (\pm 0.5)$  was discharged through the orifice and the volume of air entrained determined in the manner previously detailed †. In subsequent experiments, air was discharged through the orifice at temperatures of approximately  $100^\circ \text{C.}$  and  $184^\circ \text{C.}$ , steam and aniline vapour being, in the two cases, passed through all the jackets,  $J_1$ ,  $J_2$ ,  $J_3$ , and K. The results obtained served to determine accurately to within 1 per cent., the dependence of the discharge of air through the orifice upon the density of the air, and were employed in subsequent calculations to determine the respective discharges through the orifice, of hydrogen, coal gas, and carbon dioxide under pressures ranging from 0 to 25 cm. of water. The air-entrainment determinations with these three latter gases were made in a slightly different manner from those in the

\* Phil. Mag. *loc. cit.* p. 983.

† Phil. Mag. *loc. cit.* pp. 970-972.



case of air. The gases carbon dioxide and coal gas were stored in a large glass aspirator, and were dried by passage over calcium chloride before being delivered to the discharge tube. The pressure at the orifice fell gradually, and simultaneous readings were taken of the pressure at the orifice and the anemometer reading. The discharge of gas was then calculated from the results for air at the corresponding temperature, using the value of the specific gravity of the dry gas sampled from the aspirator, determined by an effusion method, and also, for comparison, calculated from the analysis of the sampled gas in a Bone and Wheeler gas analysis apparatus. In the case of hydrogen a somewhat similar procedure to this was followed, the gas being delivered from a high pressure cylinder and the pressure at the orifice controlled and maintained constant by means of a double reduction pressure regulator supplied by the British Oxygen Company, Ltd.

In subsequent series of experiments, the various jackets were heated to different temperatures, in order to determine the effect produced upon air entrainment by a variation of the density of the medium into which the jet issued.

### *Results and Discussion.*

The mean diameter of the orifice employed was 0.0884 cm. and the corresponding area 0.00614 sq. cm. It was circular and cylindrical to within 0.4 per cent. of its diameter and was punched in a disk of nickel steel (40 per cent. nickel) of thickness 0.0305 cm. The coefficient of linear expansion was about  $6 \times 10^{-6}$  per °C.

#### *(1) Discharge of Air at Different Temperatures.*

Fig. 2 shows how the volume of air discharged (reduced in every case to 0°C. and 760 mm. pressure) depends on the excess pressure at the orifice and the temperature of the gas when all the jackets were heated to the same temperature. Logarithms of the discharge are plotted as ordinates against the logarithms of the corresponding pressures as abscissæ, and the "best fitting" straight line drawn through the observations in each case\*. The results are expressed analytically in Table I., where formulæ derived as previously explained are given for the respective volume discharges (reduced to 0°C. and 760 mm.) in terms of the excess pressure,  $\epsilon$  cm. of water, at the orifice.

\* Phil. Mag. *loc. cit.* pp. 974-978.

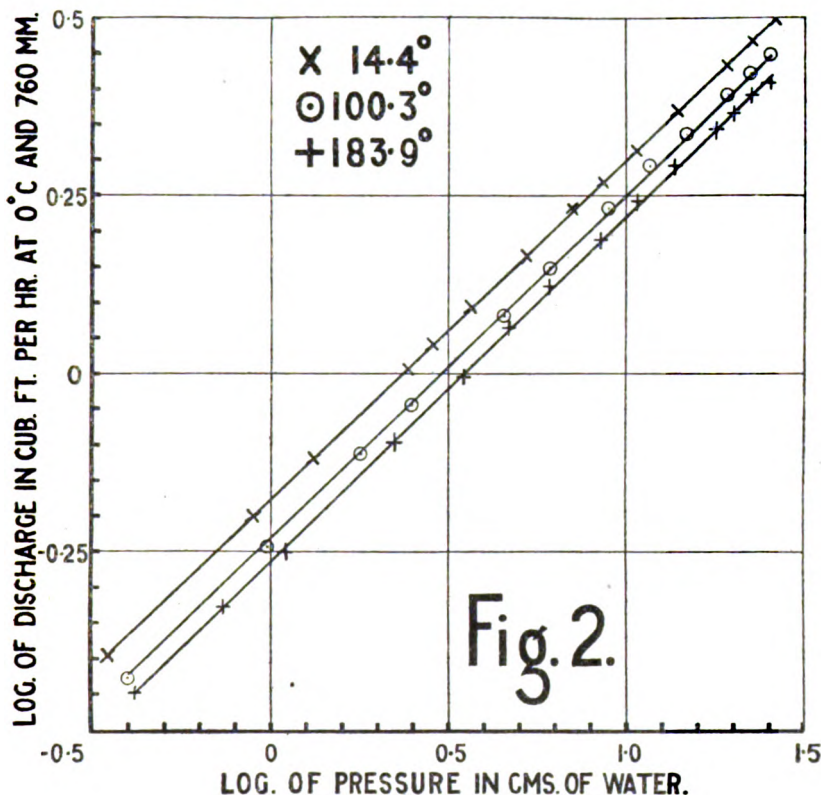


TABLE I.

Temp. of Discharge. ° C.	Empirical formula for discharge in c.c. per sec. reduced to 0°C. and 760 mm. $V = Ae^a.$	Corresponding best value of K in $V = S' \left( \frac{2eg\rho_1}{\rho_0} \right)^{\frac{1}{2}} \left( 1 - \frac{K\epsilon}{\rho} \right)^{\frac{1}{2}}$	$S'$ sq. cm.	Contraction Coefficient of jet.
14.4	$5.250480$	3.3	0.00436	0.710
100.3	$4.650482$	3.0	0.00437	0.711
183.9	$4.240486$	2.3	0.00440	0.717

We see from the fifth column that the coefficient of contraction of the jet increased by only about 1 per cent. for an increase of temperature of 160°C. To within this

degree of accuracy, the rate of discharge of air (reduced to 0° C. and 760 mm.) through the orifice at a definite excess pressure was proportional to the square root of the density of the air discharged. Within the limits of experimental error the temperatures of the jackets  $J_1$  and  $J_2$  were without influence upon the measured discharge of air. A similar degree of accuracy was obtained between the density of carbon dioxide determined from that of air by an effusion test\* and that calculated from analysis of the gas. In the case of coal gas and hydrogen, the difference between experimental and calculated values of the specific gravities relative to air were somewhat greater (1.5 per cent. and 2.5 per cent. respectively). The discharge of these gases at any definite excess pressure has therefore been calculated by means of a formula of the type given in the third column of Table I., employing the appropriate value of the specific gravity of the dry gas determined from the result of an effusion test in which the mean value of the pressure at the orifice was about 12 cm. of water. Thus, *e. g.*, for carbon dioxide (98.63 per cent.  $\text{CO}_2$ ; 0.28 per cent.  $\text{O}_2$ ; and 1.09 per cent.  $\text{N}_2$ ) at 13°·7 C. and 758.7 mm. pressure, density 0.001967 grm. per c.c. at 0° C. and 760 mm., we use  $V = 4.248 \sqrt{\epsilon} (1 - 0.0032 \epsilon)^{\frac{1}{2}}$ , the discharge  $V$  being measured at N.T.P.

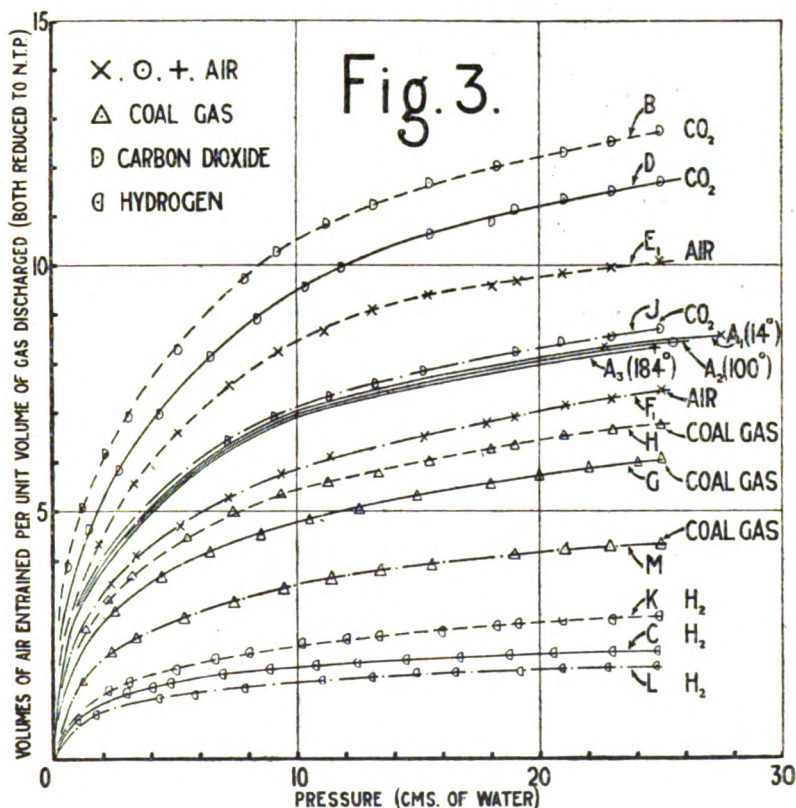
## (2) *Air entrainment by the Jet.*

Some of the results obtained for air entrainment by jets of the various gases are shown in fig. 3. Abscissæ represent pressures at the orifice, measured in cm. of water, and the ordinates represent the volumes of air entrained per unit volume of gas issuing in the jet, both volumes being reduced to 0° C. and 760 mm. pressure. We may conveniently describe the ordinates as representing the "aeration" of the jet.

We would first of all direct attention to the three curves  $A_1$ ,  $A_2$ , and  $A_3$ , representing the "aeration" of a jet of air at various pressures when discharged at temperatures equal to 14°·4 C., 100°·3 C., and 183°·9 C. respectively, the jet issuing into air at very approximately its own temperature, *i. e.*, so that the density of the air in the jet and into which the jet issues are, at least, very approximately equal. The curves referred to represent the results of experiments in which water, steam, and aniline respectively flowed through *all* the

\* See also Edwards, Tech. Paper, No. 94, Bureau of Standards, Washington.

jackets shown in fig. 1. It will be noticed that in each case (and the result is seen to hold generally), the degree of air entrainment effected by the jet increased at first very rapidly and then more slowly as the pressure at the orifice was increased. Similar results were obtained in the case of the experiments detailed in the previous communication.



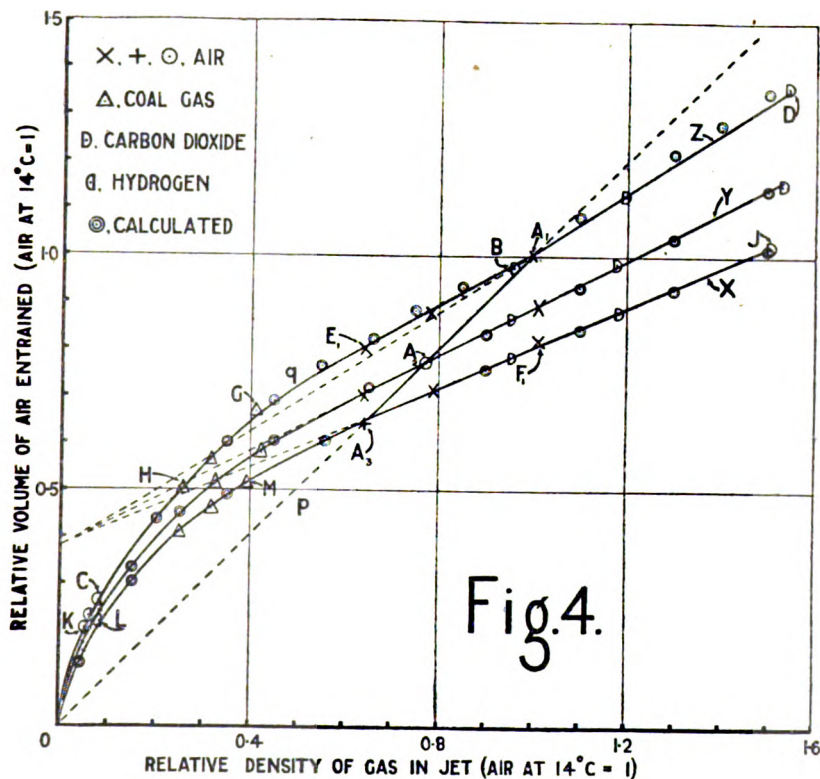
This result is not in agreement with the fundamental result quoted in Technologic Paper No. 193 (1921) of the Bureau of Standards\*, wherein it is stated that "over the range of pressure from 2 to 6 inches, the ratio of the momentum of the gas stream to the momentum of the air-gas mixture is practically a constant." It is easily shown that on this basis, the degree of air entrainment effected by the jet would be independent of the pressure.

\* *Loc. cit.* p. 25.

The curves  $A_1$ ,  $A_2$ , and  $A_3$  indicate that when a jet of air issues into air of the same density as that in the jet, the volumes of air entrained at any definite pressure per unit volume of air in the jet (both volumes being reduced to N.T.P.) is practically constant and independent of the density of the air. The curves indicate a decrease of only about 1 per cent. in the percentage aeration of the jet when the temperature of the jet and of the air into which it issued was raised from  $14^{\circ}4$  C. to  $183^{\circ}9$  C. The decrease is somewhat greater than the estimated experimental error. It will be noticed that this percentage decrease is of the same magnitude as the percentage increase in the contraction coefficient of the jet when the temperature was raised (see Table I.). Owing to this increase in value of the contraction coefficient, the surface area associated with unit volume of the jet (reduced to N.T.P.) will be diminished by approximately 1 per cent. when the temperature of the jet is raised to  $183^{\circ}9$  C. Assuming that air entrainment is effected at the surface of the jet, and is proportional to the surface area, it follows that an increase of the contraction coefficient would be accompanied by an equal percentage decrease of aeration of the jet, a deduction which is in accord with the results of the present experiments.

Results obtained when a gas issues under pressure from an orifice into air of less or greater density than the gas in the jet may be illustrated by reference to the curves D and C, which refer to the gases carbon dioxide and hydrogen respectively, the jet of each issuing at  $14^{\circ}4$  C. into air at the same temperature. It will be seen that in the case of the heavier gas (carbon dioxide), the aeration of the jet at all pressures is considerably greater than that effected in the case of a jet of air, while in the case of hydrogen, the aeration is similarly considerably smaller. The following procedure was finally adopted for representing in a concise manner the whole of the results obtained. Considering any pair of curves whatsoever, *e. g.*, curves  $A_1$  and B, referring respectively to a jet of air  $14^{\circ}4$  C. and a jet of carbon dioxide at  $183^{\circ}9$  C. discharged in each case into air at  $14^{\circ}4$  C., it was found that the ratio of the respective ordinates of the pair, corresponding to any definite excess pressure at the orifice, was practically a constant throughout the range of pressures employed. This result was found to hold in all cases, and in order to utilize it generally in the case of jets at the same or different temperatures the following procedure was adopted. The respective aerations corresponding to pressures 2, 5, 10, 15,

20, and 25 cm. were read off from the appropriate curve in fig. 3. From these values were calculated the respective degrees of air entrainment effected per unit volume of gas in the jet, reduced to the actual temperature and pressure (barometric) in the jet. The ratios of the respective degrees of air entrainment so calculated to the corresponding degree of aeration effected by a jet of air at  $14^{\circ}\cdot4$  C., issuing into



air at  $14^{\circ}\cdot4$  C., taken as a standard, were calculated, and the mean value of the resulting ratio determined. The value so calculated was plotted (see fig. 4) as ordinate against the density of the gas in the jet (under the experimental conditions of temperature and pressure) as abscissa. The procedure will be made clear by consideration of the curves  $A_1$  and B referred to above. (See Table II.)



TABLE II.

Pressure (cms. of water).	Air at 14°·4 C. (Bar. 750·6 mm.) issuing into air at 14°·4 C.		Carbon dioxide at 183°·9 C. (Bar. 767 mm.) issuing into air at 14°·4 C.		Ratio. $\beta/a$ .
	Vol. of air entrained per unit vol. of jet (both vols. reduced to N.T.P.).	Vol. of air (reduced to N.T.P.) entrained per unit vol. of jet under experi- mental conditions. (a).	Vol. of air entrained per unit vol. of jet (both vols. reduced to N.T.P.).	Vol. of air reduced to N.T.P. entrained per unit vol. of jet under experi- mental conditions. ( $\beta$ ).	
2	4·00	3·76	6·10	3·68	0·978
5	5·52	5·17	8·20	4·94	0·955
10	7·00	6·56	10·50	6·33	0·965
15	7·64	7·16	11·57	6·98	0·975
20	8·05	7·54	12·23	7·37	0·977
25	8·41	7·88	12·75	7·69	0·976
					Mean 0·971

Density of carbon dioxide and air under experimental conditions—0·001164 and 0·001214 gm. per. c.c. respectively.  
Ratio of densities ( $\text{CO}_2/\text{air}$ ) = 0·959.

The value 0·971 for the relative aeration and 0·959 for the relative density of  $\text{CO}_2$  are respectively plotted as ordinate and abscissa, and the point B in fig. 4 thus obtained. The

same procedure was followed in all other cases, air at  $14^{\circ}4$  C., issuing into air at  $14^{\circ}4$  C., being throughout made the standard for comparison of density and aeration. It will be noticed that at  $183^{\circ}9$  C. the density of the carbon dioxide in the jet (0.001164) is not very different from that of the air into which it issues (0.001214). The fact that the curves  $A_1$ ,  $A_2$ , and  $A_3$  are almost coincident in fig. 3 indicates that results derived from these curves plotted in fig. 4 as described must yield points  $A_1$ ,  $A_2$ , and  $A_3$ , lying practically on a straight line passing through the origin. We may say, therefore, that in the case of a jet of air issuing into air of the same density, the volume of air (reduced to N. T. P.) entrained by the jet per unit volume of the jet measured under the experimental conditions of temperature and pressure is strictly proportional to the actual density of the gas under these latter conditions. That this is so for jets of gases other than air issuing into air of the same density as the jet, is seen from the position of the point B corresponding to carbon dioxide issuing at  $183^{\circ}9$  C. into air at  $14^{\circ}4$  C. (respective densities 0.001164 and 0.001214). B lies very nearly on the line  $A_1 A_2 A_3$ , and only slightly above the corresponding point having the same abscissa on this line. The slight deviation of the position of B from this line is, as will be seen later, in the direction attributable to the slight defect of the density of the carbon dioxide from that of the air into which it issues.

Curve C in fig. 3 refers to a jet of hydrogen at  $14^{\circ}4$  C. issuing into air at the same temperature, and curve D to a jet of carbon dioxide issuing into air under the same condition. The corresponding points in fig. 4 are represented by C and D respectively. It will be seen that in the case of the lighter gas (hydrogen) issuing into a heavier gas (air) the value of the ordinate (point C) in fig. 4 is greater than the value to be anticipated on the assumption that the volume of air entrained per unit volume of the issuing gas (measured under experimental conditions) is proportional to the density of the gas. In the case of a heavier gas (carbon dioxide) issuing into a lighter gas (air) the actual aeration is less than that anticipated on this assumption. Clearly then the degree of aeration of a jet is affected not only by the density of the gas in the jet but also by the density of the medium into which the jet issues. In order to examine this point in detail, experiments were carried out in which the gas flowing through the jet orifice was maintained at various temperatures ( $14^{\circ}4$ ,  $100^{\circ}$  C. or  $183^{\circ}9$  C.) while the air entrained was raised to the same or a different temperature



by delivery of cold water ( $14^{\circ}\cdot4$  C.), steam, or aniline vapour to the jackets  $J_1$ . Thus in fig. 3 curves  $A_1$ ,  $E_1$ , and  $F_1$  refer to air entrainment by a jet of air at  $14^{\circ}\cdot4$  C.,  $184^{\circ}$  C., and  $14^{\circ}\cdot4$  C., while the air entrained was at temperatures respectively equal to  $14^{\circ}\cdot4$  C.,  $14^{\circ}\cdot4$  C., and  $184^{\circ}$  C. Similar results for the same temperatures are shown for coal gas, carbon dioxide, and hydrogen by the curves  $G$ ,  $H$ ,  $M$ ;  $D$ ,  $B$ ,  $J$ ; and  $C$ ,  $K$ ,  $L$  respectively. The corresponding points are similarly represented by the appropriate letter in fig. 4, in which various other results in addition to those shown in fig. 3 are plotted. The curves  $X$ ,  $Y$ , and  $Z$  thus refer respectively to results obtained when the temperature of the air into which the jet of gas issued was respectively  $183^{\circ}\cdot9$  C.,  $100^{\circ}$  C., and  $14^{\circ}\cdot4$  C. The result referred to above is seen to be applicable to the whole of the results. Thus considering the curve  $Y$  referring to discharge of gas into air at  $100^{\circ}$  C., it is seen that  $Y$  and the straight line  $A_1 A_2 A_3$  intersect accurately at the point  $A_2$ , corresponding to conditions of equal density of the issuing gas and of the medium into which the gas issues. For values of the density of the issuing gas greater than that of the air at  $100^{\circ}$  C. into which it issues, ordinates of the curve  $Y$  are less than the corresponding ordinate of the straight line  $A_1 A_2 A_3$ . Similarly for values of the density of the issuing gas less than that represented by  $A_2$ , ordinates of  $Y$  are greater than the corresponding ordinates of  $A_1 A_2 A_3$ . A similar result is seen to hold when the jet of gas issues into air at  $14^{\circ}\cdot4$  C. or  $183^{\circ}\cdot9$  C.

These results may be satisfactorily explained as follows :— A jet of gas issuing into air or other gaseous medium is differentiated from a liquid jet issuing into a liquid or gas in that while in the latter case the surface of the jet is well defined, and the properties of the jet determined very largely by surface tension and density considerations \*, in the case of the gas jet forces due to surface tension are practically entirely absent. Moreover, considerations of the respective densities of the issuing gas and of the medium into which the gas issues are of increased importance owing to the possibility of a process of diffusion occurring at the surface of the gas jet. In the case of these respective densities being equal, such a process of diffusion will be absent, but an analogous effect is produced by a process of interchange between the jet and the surrounding medium. Consider, however, the case of a gas of density  $\rho_1$  issuing into a gas of different

\* See *e. g.*, Smith and Moss, *Proc. Roy. Soc.* 1917, A. xciii., 373.

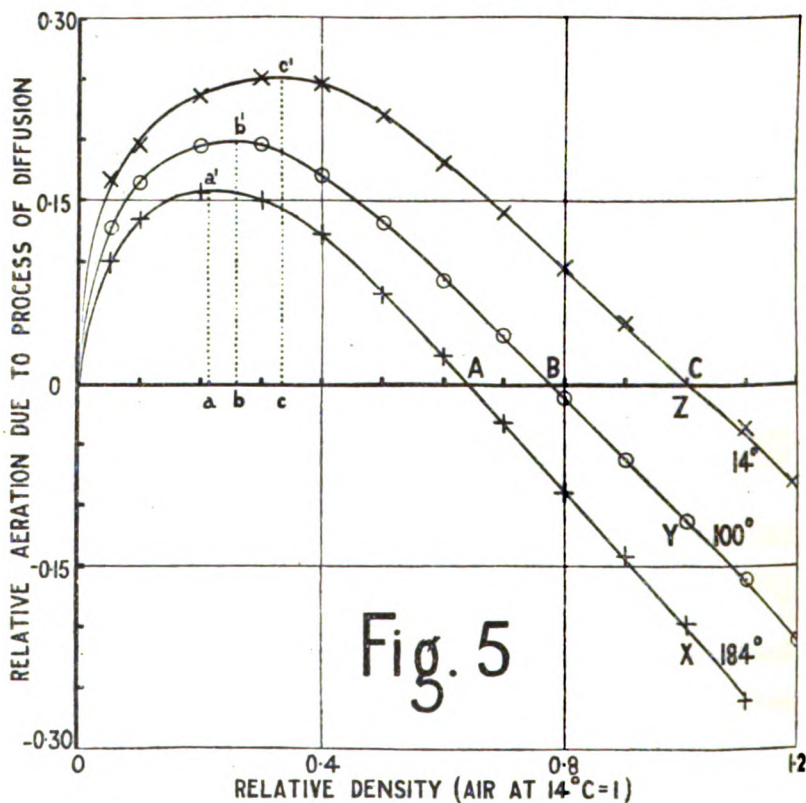
density  $\rho_2$ , at any pressure. Let a fraction,  $\beta$ , of each unit volume of gas discharged diffuse into the surrounding medium. It can easily be seen that the fraction will be, at any definite pressure, at least approximately constant, for, whatever the density of the gas, both the velocity of diffusion of the gas into the surrounding medium and the velocity of discharge of the gas from the orifice at any pressure are inversely proportional to the square root of the density of the gas, and the ratio is therefore a constant. The former velocity is a measure of the tendency of the gas to leave the jet, and the latter is a measure of the tendency of the gas to be retained in the jet. The present assumption of constancy in the value of  $\beta$  will be shown later to be in accord with the experimental results. Consider a volume  $V$  of gas discharged in the jet. A volume  $\beta V$  of this gas diffuses into the surrounding gas, and likewise a volume of  $\beta V \sqrt{\rho_1/\rho_2}$  of the surrounding gas diffuses into the jet. This diffusion process will continue until a state of equal densities is attained in the jet and the surrounding medium. The volume of gas in the jet becomes  $V - \beta V + \beta V \sqrt{\rho_1/\rho_2}$  and the mass is  $(V - \beta V)\rho_1 + \beta V \sqrt{\rho_1\rho_2}$ . The effective density of the gas is therefore

$$[(V - \beta V)\rho_1 + \beta V \sqrt{\rho_1\rho_2}]/(V - \beta V + \beta V \sqrt{\rho_1/\rho_2}).$$

Expanding as far as the first power of  $\beta$  this expression after a little algebraic reduction gives for the effective density of the jet the value  $\rho_1 + \beta(\rho_2 - \rho_1)(\rho_1/\rho_2)^{\frac{1}{2}}$ . The result of a process of the nature of diffusion is to increase the effective density of the jet when the jet issues into a medium of high density ( $\rho_2 > \rho_1$ ), and to reduce the effective density when the jet issues into a lighter medium, ( $\rho_2 < \rho_1$ ). The magnitude of such increased or decreased density is, so far as the first power of  $\beta$  is concerned, equal to  $\beta(\rho_2 - \rho_1) \times (\rho_1/\rho_2)^{\frac{1}{2}}$ . In the equilibrium state the jet issues into a medium of equal density, and as under these conditions the degree of air entrainment is strictly proportional to the density of the gas in the jet (see p. 795), we may say that the increased degree of air entrainment effected due to a process of the nature of diffusion is given by  $\alpha\beta(\rho_2 - \rho_1)(\rho_1/\rho_2)^{\frac{1}{2}}$  where  $\alpha$  is a constant. The correctness of this result and the limits—if any—within which the formula is valid can be readily tested by means of the experimental data contained in fig. 4. The form of the expression is seen to be in accord with experimental anticipations, for the expression vanishes when  $\rho_1 = 0$  and when  $\rho_1 = \rho_2$ . Moreover, for  $\rho_2 \rightarrow 0$ , i. e., in the case of a gas issuing into an evacuated vessel, the

expression assumes a large negative value, indicating complete withdrawal of all the gas initially from the jet.

In fig. 5 data derived from fig. 4 as follows have been plotted. Corresponding to any definite abscissa, *e. g.*, 0.5 in fig. 4, the difference  $pq$  of the respective ordinates of the curve Z and the straight line  $A_1A_2A_3$  was determined and plotted in fig. 5 as ordinate against the density of the gas in



the jet (relative to air at 14° C. and 760 mm.), *i. e.*, 0.5 as before. This procedure was followed in the case of each of the curves X, Y, and Z, the respective differences in the values of the ordinates from those corresponding to the straight line  $A_1A_2A_3$  being determined at intervals of 0.1 in the relative density. The curves so obtained are correspondingly represented by X, Y, and Z in fig. 5. For any individual curve the density of the air into which the jet issues ( $\rho_2$ ) is a constant. The curves exhibit the relation

between the degree of air entrainment, due to a process of the nature of diffusion occurring at the jet, and the density of the issuing gas, *i. e.*, ordinates are proportional to  $\alpha\beta(\rho_2 - \rho_1)(\rho_1/\rho_2)^{\frac{1}{2}}$ , conveniently represented by the symbol  $E$ , and abscissæ to  $\rho_1$ , while  $\rho_2$  has a constant value appropriate to the respective curves. It has been already pointed out that  $E$  vanishes when  $\rho_1 = 0$  and when  $\rho_1 = \rho_2$ . It is of interest

to examine the value of  $\frac{dE}{d\rho_1}$ . We have  $\frac{dE}{d\rho_1} = \frac{\alpha\beta(\rho_2 - 3\rho_1)}{2\sqrt{\rho_1\rho_2}}$ ,

and when  $\rho_1$  is small,  $\frac{dE}{d\rho_1}$  is very large, being equal to

$\frac{1}{2}\sqrt{\frac{\rho_2}{\rho_1}}$ . The respective curves therefore are very steep in the neighbourhood of the origin and cut the axis of abscissæ at right angles. A maximum value of  $E$  occurs when  $\rho_1 = \rho_2/3$ . Now the values of  $\rho_2$  in the case of the curves in fig. 5 are proportional to the abscissæ, OA, OB, and OC, which are respectively equal to 0.644, 0.775, and 1.00. It is seen from the curves that the respective maxima of the curves in fig. 5 correspond very closely with values of the abscissæ represented by Oa, Ob, and Oc, which are respectively equal to one third of OA, OB, and OC, a result in agreement with that just deduced from the form of the expression  $E$ . Furthermore, the respective maximum values of  $E$  corresponding with  $\rho_1 = \rho_2/3$  are given by  $2\alpha\beta\rho_2/3\sqrt{3}$ , *i. e.*, are proportional to  $\rho_2$ , assuming, as we have done, that  $\alpha$  and  $\beta$  are constants. The experimental values of the maximum ordinates  $aa'$ ,  $bb'$ , and  $cc'$  are found, from the curves in fig. 5, to be in the ratio 0.640 : 0.784 : 1.000 in very close agreement with the corresponding ratio of OA, OB, and OC, viz. 0.644 : 0.775 : 1.000. The assumption of the constancy of  $\beta$  therefore appears to be justified at least so far as these values are concerned. Calculating the value of  $\beta$  from these maximum values of  $E$ , we find from the curves X, Y, and Z the respective values 0.646, 0.659, and 0.649 for  $\beta$ . Taking the mean of these we find  $E = 0.651\alpha(\rho_2 - \rho_1)\sqrt{\rho_1/\rho_2}$ . Hence the relative degree of air entrainment effected by the jet is given by  $V = \alpha[\rho_1 + 0.651(\rho_2 - \rho_1)\sqrt{\rho_1/\rho_2}]$ . It will be seen from fig. 4 that for values of the density of the gas into which the jet issues greater than that of the issuing gas, values of the aeration calculated by means of this formula are in very close agreement with the experimental values. In cases where the issuing gas is heavier than that into which it issues, the formula affords values of the air entrainment lower than the experimental values. In this

latter case, the experimental values indicate that a linear relation exists between the degree of air entrainment due to diffusion and the density of the issuing gas. These relations for the cases when a relatively heavier gas issues into air at 14°·4 C., 100° C., and 184° C. respectively are given in Table III. herewith.

TABLE III.

Relation of E, the relative air entrainment due to diffusion effected by a jet of gas issuing into a relatively lighter medium.

Temperature of air into which jet issues.	Density relative to air at 14° C. and 760 mm.	Linear relation for $E = -(\gamma\rho_1 + \delta)$ .
14°·4 C.	1·000	$-(0·623\rho_1 + 0·38)$
100° C.	0·775	$-(0·508\rho_1 + 0·38)$
184° C.	0·644	$-(0·420\rho_1 + 0·38)$

It is found that the three values of  $\gamma$  given in the third column of the above table are expressed very approximately in terms of the respective values of  $\rho_2$  by the linear relation  $\gamma = 0·65\rho_2$  and hence in the case of a jet of gas of density  $\rho_1$  issuing into a lighter gas of density  $\rho_2$ , the degree of air entrainment effected is given by  $V = \alpha[\rho_1 - (0·65\rho_1\rho_2 + 0·38)]$ . It is interesting to note that the value of the constant 0·65 in this equation is practically the same as that occurring in the relation already deduced for air entrainment effected by a jet of gas issuing into a denser medium (see page 799). This factor and " $\alpha$ " are most probably instrumental constants appropriate to the form of orifice employed, and the dimensions and disposition of the flow system through which the stream of air induced by the jet flows.

#### Summary.

1. A form of apparatus employing a hot-wire anemometer for the determination of the relative amounts of air entrained by jets of various gases and permitting the densities both of the gas issuing in the jet and that entrained by the jet to be varied within wide limits, is described.

2. It is shown that to within a possible error of 1 per cent. the rate of discharge of air (reduced to 0° C. and 760 mm.) through the orifice employed at a definite excess pressure is

proportional to the square root of the density of the air discharged.

3. When a gas jet issues into air of equal density, the volume of air entrained per unit volume of gas delivered in the jet is strictly proportional to the density of the gas discharged.

4. When the density of the issuing gas is not equal to that of the gas into which it issues, the relation given under (3) no longer applies. In this case the relation between the respective densities of the two gases and the degree of air entrainment effected by the jet is different according as the jet issues into a gas of lower or higher density.

5. In the case of a lighter gas issuing into a heavier gas the volume of air entrained (reduced to N.T.P.) per unit volume of gas issuing in the jet (measured under the experimental conditions of temperature and pressure) is given by  $V = \alpha[\rho_1 + \beta(\rho_2 - \rho_1)(\rho_1/\rho_2)^{\frac{1}{2}}]$ , where  $\alpha$  is the volume of air entrained by a jet of air of standard density, taken as the unit, issuing at the same excess pressure into air of equal density,  $\beta$  is a constant, and  $\rho_1$  and  $\rho_2$  denote respectively the densities of the issuing gas and that of the gas into which the jet issues.

6. The relation given in (5) is deduced on the assumption that a process somewhat analogous to diffusion occurs between the jet and the surrounding medium, and that the result given under (3) is applicable to air entrainment by a jet of gas the density of which tends to become equal to that of the surrounding medium by such process.

7. In agreement with the experimental results, the formula in (5) indicates that air entrainment due to such process of diffusion is a maximum when the density of the issuing gas is one third of that into which the gas issues.

8. In the case of a jet of gas issuing into a lighter medium the corresponding relation for  $V$  takes the form  $V = \alpha[\rho_1 - (\beta\rho_1\rho_2 + c)]$ , where  $\alpha$  and  $\beta$  have the same values as in (5) above, and are, it is suggested, instrumental constants, and  $c$  is an additional constant.

The work detailed herein was carried out in the Physical Laboratory of the South Metropolitan Gas Company, and the authors desire to express their thanks to Dr. Charles Carpenter and the Directors for their ready provision of all facilities necessary to carry out the work, and for permission to publish the same.

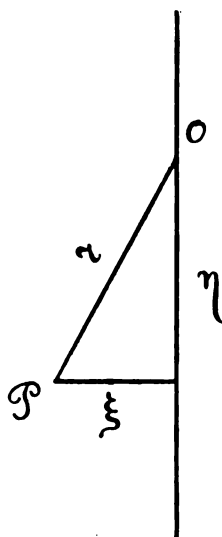
South Metropolitan Gas Company,  
700 Old Kent Road, S.E. 15.  
July 25, 1923.

LXXXIX. *Diffraction Image of Two Close Luminous Planes.*

By B. E. MOURASHKINSKY, *Optical Laboratory of the Central Chamber of Weights and Measures, Petrograd* \*.

THE problem of the resolution of two luminous planes is the same as that of the diffractive conditions of the visibility of a band of finite width on a bright background. The resolving power of an object-glass for two luminous planes depends on the distribution of illumination in the diffraction image of these planes. The illumination at any point in the diffraction image of two planes due to a circular aperture can be expressed in the following manner.

Fig. 1.



The illumination at the point P (fig. 1) in the diffraction image of a point light source is expressed by

$$I_P = \frac{\pi^2 R^4}{\lambda^2 f^2} \cdot \frac{4J_1^2(x)}{x^2}, \quad \dots \quad (1)$$

where

$$x = \frac{2\pi R}{\lambda f} \cdot r, \quad \dots \quad (2)$$

$r$  being the distance of the point P from O, the geometrical image of a point source.

\* Communicated by the Author.

Integrating (1) with respect to  $\eta$  from  $-\infty$  to  $+\infty$ , we obtain the illumination at the point P due to a narrow line of width  $d\xi$ . The expression for this integral was obtained by H. Struve\* and by Lord Rayleigh†, it is

$$I_l = C_1 \frac{\pi^2 R^4}{\lambda^2 f^2} d\xi \int_{-\infty}^{+\infty} \frac{4J_1^2(x)}{x^2} d\eta = C_1 2R \int_{-\infty}^{+\infty} \frac{J_1^2(x)}{x \sqrt{x^2 - z^2}} dx, \quad (3)$$

where

$$\eta^2 = r^2 - \xi^2;$$

$$\xi = \frac{\lambda f}{2\pi R} z;$$

$$d\eta = \frac{r dr}{\eta} = \left( \frac{\lambda f}{2\pi R} \right)^2 \frac{x dx}{\eta}, \quad (4)$$

$\xi$  being the linear distance of the point P from the geometrical image of a line source.

The integral (3) is calculated by means of the Struve function  $H_1(z)$ ,

$$H_1(z) = \frac{2z^2}{\pi} \int_0^{\pi} \sin(z \sin \theta) \cos^2 \theta d\theta \\ = \frac{2}{\pi} \left[ \frac{z^3}{1^2 \cdot 3} - \frac{z^5}{1^2 \cdot 3^2 \cdot 5} + \frac{z^7}{1^2 \cdot 3^2 \cdot 5^2 \cdot 7} - \dots \right]. \quad (5)$$

The function  $H_1(z)$  used here is the same as Gray and Mathews‡ used in their exposition of Struve's results, it differs from the Struve function  $H_1(z)$ . The relation between the two functions is

$$\underset{\text{Gr.}}{H_1(z)} = \underset{\text{St.}}{H_1(z)} z.$$

By means of (5) Struve has found that

$$I_l = C_1 2R^2 \frac{2H_1(2z)}{(2z)^3} dz. \quad (6)$$

If we want to express the illumination at the point P in terms of illumination at the geometrical image of a line

\* *Mémoires de l'Académie des Sciences de St. Petersburg*, xxx. no. 8 (1882); *Ann. der Phys.* xvii. p. 1008 (1882).

† "Wave Theory," *Encyclopedia Britannica*.

‡ Gray and Mathews, 'Treatise on Bessel's functions,' p. 213 (1922). Our expressions for the constants  $C_1$  and  $C_2$  differ from those of Struve and Gray and Mathews, as they omit the constant factor in the expressions (1) and (9).



source ( $z=0$ ), assumed to be equal to unity, we obtain by means of (5)

$$\frac{2H_1(2z)}{(2z)^3} = \frac{H_1(2z)}{4z^3} = \frac{4\pi}{3} \quad . \quad . \quad . \quad (7)$$

$$z = 0$$

and

$$I_l = C_1 \frac{2R^2 \cdot 2H_1(2z)}{(2z)^3} = C_1 2R^2 \frac{4}{3\pi} dz = 1. \quad . \quad (8)$$

$$z = 0$$

Thus the constant  $C_1$  is determined as

$$C_1 = \frac{3\pi}{8R^2 dz},$$

and (6) takes the form

$$I_l = \frac{3\pi}{4} \cdot \frac{H_1(2z)}{4z^3} = \frac{3\pi}{2} \cdot \frac{H_1(2z)}{(2z)^3} \quad . \quad . \quad . \quad (9)$$

If we denote with Lord Rayleigh,

$$L(z) = \frac{\pi}{2} \frac{H_1(2z)}{(2z)^3}, \quad . \quad . \quad . \quad (10)$$

we can write

$$I_l = 3L(z). \quad . \quad . \quad . \quad (11)$$

The function  $L(z)$  by means of (5) can be represented by the series

$$L(z) = \frac{1}{1^2 \cdot 3} - \frac{(2z)^2}{1^2 \cdot 3^2 \cdot 5} + \frac{(2z)^4}{1^2 \cdot 3^2 \cdot 5^2 \cdot 7} - \dots \quad (12)$$

If we have to determine the illumination at the point P due to an infinite luminous plane bounded by a straight edge, we can use the following expressions obtained by Struve:

$$I_s = C_2 3 \int_z^\infty L(z) dz, \quad . \quad . \quad . \quad (13)$$

$z$  is equal, as before, to  $\frac{2\pi R}{\lambda f} \cdot r$ , where  $r$  is the distance of the point P from the geometrical image of the edge. The constant  $C_2$  is determined, if the sought illumination at the point P is expressed in terms of illumination at the same point due to the luminous plane of the same brightness and infinite in all directions. The illumination of the latter is

assumed to be equal to unity, the illumination at the geometrical image of the edge is half of that.

Then

$$I_s = 3 \cdot C_2 \int_z^\infty L(z) dz \Big|_{z=0} = 3 \cdot C_2 \int_0^\infty L(z) dz,$$

and by (5) and (9) it is equal

$$\frac{3\pi^2}{16} C_2 = \frac{1}{2},$$

where from

$$C_2 = \frac{8}{3\pi^2} \dots \dots \dots (14)$$

and

$$I_s = \frac{8}{\pi^2} \int_z^\infty L(z) dz, \dots \dots \dots (15)$$

or

$$\begin{aligned} I_s &= \frac{8}{\pi^2} \int_0^\infty L(z) dz - \frac{8}{\pi^2} \int_0^z L(z) dz \\ &= \frac{1}{2} - \frac{8}{\pi^2} \int_0^z \left[ \frac{1}{1^2 \cdot 3} - \frac{(2z)^2}{1^2 \cdot 3^2 \cdot 5} + \frac{(2z)^4}{1^2 \cdot 3^2 \cdot 5^2 \cdot 7} - \dots \right] dz \\ &= \frac{1}{2} - \frac{2}{\pi} \sum_{n=1}^{\infty} (-1)^{n-1} \frac{2n+1}{2n-1} \cdot \frac{2^{2n}}{(1 \cdot 3 \cdot 5 \dots 2n+1)^2} z^{2n-1}. \end{aligned} \quad (16)$$

From this

$$I_s(+z) + I_s(-z) = 1, \dots \dots \dots (17)$$

where  $I_s(+z)$  refers to the point outside of the geometrical image of a luminous plane and  $I_s(-z)$  refers to the point inside of it at the distance  $z$  from the image of the edge.

For the expression (15) we have the Struve tables.

If we have a band of width  $D$ , where

$$D = \frac{2\pi R}{\lambda f} d, \dots \dots \dots (18)$$

$d$  being a linear width of the geometrical image of a band in the focal plane, the illumination at the point  $P$  at the distance  $z$  from an image of one (nearer to the point  $P$ ) edge of a band will be

$$I_b(+z) = \frac{8}{\pi^2} \int_z^{z+D} L(z) dz, \dots \dots \dots (19)$$

$$I_b(-z) = \frac{8}{\pi^2} \int_{-z}^{D-z} L(z) dz, \dots \dots \dots (20)$$

The  $I_b(+z)$  refers to the point outside of the image of a band,  $I_b(-z)$  to the point inside of it. These integrals can be easily calculated by means of the mentioned Struve tables in the following manner :

$$I_b(+z) = \frac{8}{\pi^2} \int_z^\infty L(z) dz - \frac{8}{\pi^2} \int_{D+z}^\infty L(z) dz, \quad (21)$$

$$I_b(-z) = \frac{8}{\pi^2} \int_{-z}^\infty L(z) dz - \frac{8}{\pi^2} \int_{D-z}^\infty L(z) dz. \quad (22)$$

All the four integrals are to be taken directly from Struve's tables. At the axis of a band ( $z = -\frac{D}{2}$ ), we have

$$I_b\left(-\frac{D}{2}\right) = \frac{8}{\pi^2} \int_{-\frac{D}{2}}^\infty L(z) dz - \frac{8}{\pi^2} \int_{+\frac{D}{2}}^\infty L(z) dz,$$

or by (17)

$$I_b\left(-\frac{D}{2}\right) = 1 - 2 \cdot \frac{8}{\pi^2} \int_{\frac{D}{2}}^\infty L(z) dz. \quad (23)$$

At the geometrical image of the edge of a band ( $z=0$ ) we have

$$\begin{aligned} I_b(0) &= \frac{8}{\pi^2} \int_0^\infty L(z) dz - \frac{8}{\pi^2} \int_D^\infty L(z) dz \\ &= \frac{1}{2} - \frac{8}{\pi^2} \int_D^\infty L(z) dz. \quad (24) \end{aligned}$$

Let us consider now the general case, namely, two luminous planes with straight edges of brightness  $a$  and  $c$  and a band between them of width  $D$  and brightness  $b$ . The illumination at the point P at the distance  $+z$  from the nearer edge *inside* of the geometrical image of a band and at the distance  $-z$  *outside* of the image of a band will be

$$\left. \begin{aligned} I(+z) &= a \frac{8}{\pi^2} \int_z^\infty L(z) dz + b \frac{8}{\pi^2} \int_{-z}^{D-z} L(z) dz \\ &\quad + c \frac{8}{\pi^2} \int_{D+z}^\infty L(z) dz, \\ I(-z) &= a \frac{8}{\pi^2} \int_{-z}^\infty L(z) dz + b \frac{8}{\pi^2} \int_z^{D+z} L(z) dz \\ &\quad + c \frac{8}{\pi^2} \int_{D-z}^\infty L(z) dz, \end{aligned} \right\} \quad (25)$$

or using the relation (17)

$$\begin{aligned} I(+z) &= b - (a-b) \frac{8}{\pi^2} \int_z^\infty L(z) dz - (c-b) \frac{8}{\pi^2} \int_{D-z}^\infty L(z) dz, \\ I(-z) &= a - (b-a) \frac{8}{\pi^2} \int_z^\infty L(z) dz + (c-b) \frac{8}{\pi^2} \int_{D+z}^\infty L(z) dz. \end{aligned} \quad (26)$$

If two planes are of equal brightness ( $a=c$ ) (26) may be written

$$\begin{aligned} I(+z) &= b + (a-b) \left[ \frac{8}{\pi^2} \int_{D-z}^\infty L(z) dz + \frac{8}{\pi^2} \int_z^\infty L(z) dz \right], \\ I(-z) &= a + (a-b) \left[ \frac{8}{\pi^2} \int_{D+z}^\infty L(z) dz - \frac{8}{\pi^2} \int_z^\infty L(z) dz \right] \end{aligned} \quad (27)$$

At the axis of a band  $\left(z = +\frac{D}{2}\right)$  we have

$$I\left(+\frac{D}{2}\right) = b + (a-b) 2 \cdot \frac{8}{\pi^2} \int_{\frac{D}{2}}^\infty L(z) dz. \quad (28)$$

At the geometrical image of one edge of a band the illumination will be

$$I(0) = (a+b) \cdot \frac{1}{2} + (a-b) \frac{8}{\pi^2} \int_D^\infty L(z) dz. \quad (29)$$

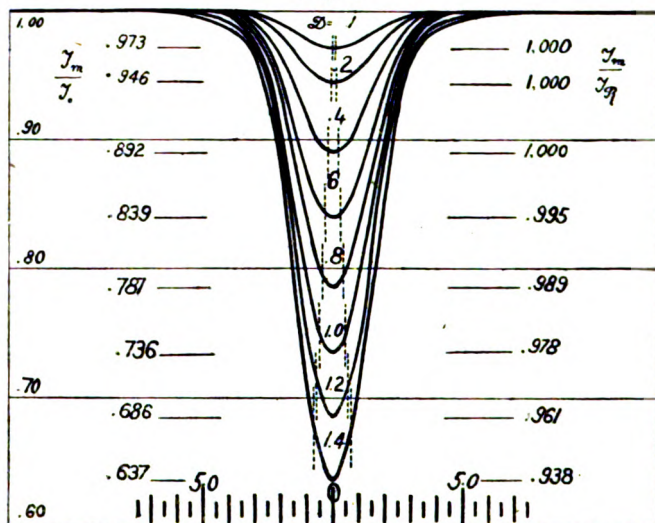
By means of (27), (28), and (29) the distribution of illumination in a focal plane of an object-glass for different values of  $b$  and for different values of  $D$  may be easily calculated.

Two luminous sources with straight edges (lines, bands, infinite planes with straight edges) have a more simple diffraction pattern in a focal plane of an object-glass than two luminous points or disks, as all the isophotes of the first are always straight lines parallel to the edge. It is sufficient to know the distribution of illumination along one line perpendicular to the edge. We calculated it by means of (27) firstly for the case of  $b=0$ , *i. e.*, for two luminous planes of equal brightness with a dark band of width  $D$  between them for different values of  $D$ , from  $D=0.1$  to  $D=5.0$ . The results for some values of  $D$  are given in fig. 2.

We shall note five characteristic points of these curves: (1) the point of minimum illumination at the axis of a

central band; (2) two points corresponding to the geometrical images of the edges; (3) two points at which the illumination differs from the general illumination but by a fraction of percentage, say at which it is equal to 0.995. The values of illumination at the axis and that at the image of the edges are given in the second columns of the Tables I. and II.

Fig. 2.



We see that the illumination at the axis for small values of  $D$  differs little from the illumination at the edges. For  $D=1.0$  and  $D=1.4$  the illumination at the axis is about 0.98 and 0.94 of that at the edges respectively, but for greater values of  $D$  this ratio decreases very rapidly, so for  $D=4.0$  and  $D=5.0$  the illumination at the axis is only about 0.36 and 0.28 of that at the edges. These values of illumination at the axis in terms of that at the edges are given in the Table III. and fig. 5. The figures of Tables I., II., III. are correct to 2-3 units of fourth decimal.

The points at which the illumination is nearly equal to general illumination for small values of  $D$  are close together, so that the distance of such points on one side of the image for  $D=0.1$  and for  $D=2.0$  is only about 4.0, i. e., it is approximately equal to the limit of resolution of the eye (for two luminous points) and practically the positions of these points on the curves may be considered as coincident.

The points of the curves on fig. 2 corresponding to the geometrical images of the edges are marked by dotted lines.

TABLE I.

D.	b = 0.	0.1.	0.2.	0.3.	0.4.	0.5.	0.6.	0.7.	0.8.	0.9.
0.1	9730	9757	9784	9811	9838	9865	9892	9919	9946	9973
0.2	9460	9514	9568	9622	9676	9730	9784	9838	9892	9946
0.4	8922	9030	9138	9245	9353	9461	9569	9677	9784	9892
0.6	8390	8551	8712	8873	9034	9195	9357	9517	9678	9839
0.8	7868	8081	8294	8508	8721	8934	9147	9360	9574	9788
1.0	7336	7620	7885	8149	8414	8678	8942	9207	9471	9736
1.2	6856	7170	7485	7799	8114	8428	8742	9057	9371	9686
1.4	6374	6737	7099	7462	7824	8187	8550	8912	9275	9634
1.6	5910	6319	6728	7137	7546	7955	8364	8773	9182	9591
1.8	5464	5918	6371	6825	7278	7732	8186	8639	9093	9546
2.0	5042	5538	6034	6529	7025	7521	8017	8513	9008	9504
2.2	4642	5178	5714	6249	6785	7321	7857	8393	8928	9464
2.4	4264	4838	5411	5985	6558	7132	7706	8279	8853	9426
2.6	3912	4521	5130	5738	6347	6956	7565	8174	8782	9391
2.8	3586	4227	4869	5510	6152	6793	7434	8076	8717	9359
3.0	3284	3956	4627	5299	5970	6642	7314	7985	8657	9328
3.2	3008	3704	4406	5106	5805	6504	7203	7902	8602	9301
3.4	2738	3481	4206	4931	5655	6379	7103	7827	8552	9276
3.6	2530	3277	4024	4771	5518	6265	7012	7759	8506	9253
3.8	2326	3063	3861	4628	5396	6163	6930	7698	8465	9233
4.0	2146	2914	3717	4502	5288	6073	6858	7644	8429	9215
4.2	1986	2787	3589	4390	5192	5993	6794	7596	8397	9200
4.4	1846	2661	3477	4292	5108	5923	6738	7554	8369	9185
4.6	1724	2552	3379	4207	5034	5862	6690	7517	8345	9172
4.8	1620	2458	3296	4137	4972	5810	6648	7485	8324	9162
5.0	1530	2377	3224	4071	4918	5765	6612	7459	8306	9153

TABLE II.

P.	b =	0.	0.1.	0.2.	0.3.	0.4.	0.5.	0.6.	0.7.	0.8.	0.9.
0.1	.....	.9730	.9757	.9784	.9811	.9838	.9865	.9892	.9919	.9946	.9973
0.2	.....	.9461	.9515	.9569	.9623	.9677	.9730	.9784	.9838	.9892	.9946
0.4	.....	.8934	.9041	.9147	.9254	.9360	.9467	.9574	.9680	.9787	.9893
0.6	.....	.8428	.8585	.8742	.8900	.9057	.9214	.9371	.9528	.9686	.9843
0.8	.....	.7955	.8160	.8364	.8568	.8773	.8978	.9182	.9386	.9591	.9796
1.0	.....	.7521	.7769	.8017	.8265	.8513	.8760	.9008	.9256	.9504	.9752
1.2	.....	.7132	.7419	.7706	.7992	.8279	.8566	.8853	.9140	.9426	.9713
1.4	.....	.6793	.7114	.7434	.7755	.8076	.8396	.8717	.9038	.9359	.9679
1.6	.....	.6504	.6854	.7203	.7553	.7902	.8252	.8601	.8951	.9301	.9650
1.8	.....	.6265	.6638	.7012	.7386	.7759	.8132	.8506	.8880	.9253	.9626
2.0	.....	.6073	.6466	.6858	.7251	.7644	.8036	.8429	.8822	.9215	.9607
2.2	.....	.5923	.6361	.6738	.7146	.7554	.7962	.8369	.8777	.9185	.9592
2.4	.....	.5810	.6229	.6648	.7067	.7486	.7905	.8324	.8743	.9162	.9581
2.6	.....	.5728	.6155	.6582	.7010	.7437	.7864	.8291	.8718	.9146	.9573
2.8	.....	.5670	.6103	.6536	.6969	.7402	.7835	.8268	.8701	.9134	.9567
3.0	.....	.5630	.6067	.6504	.6941	.7378	.7815	.8252	.8689	.9126	.9563
3.2	.....	.5602	.6042	.6482	.6921	.7361	.7801	.8241	.8681	.9120	.9560
3.4	.....	.5581	.6023	.6465	.6907	.7349	.7790	.8232	.8674	.9116	.9558
3.6	.....	.5564	.6008	.6451	.6895	.7338	.7782	.8226	.8669	.9113	.9556
3.8	.....	.5547	.5992	.6438	.6883	.7328	.7774	.8219	.8664	.9109	.9555
4.0	.....	.5528	.5975	.6422	.6870	.7317	.7764	.8211	.8658	.9106	.9553
4.2	.....	.5506	.5955	.6405	.6854	.7304	.7753	.8202	.8652	.9101	.9551
4.4	.....	.5484	.5936	.6387	.6839	.7290	.7742	.8194	.8645	.9097	.9548
4.6	.....	.5459	.5913	.6367	.6821	.7273	.7726	.8178	.8638	.9092	.9546
4.8	.....	.5434	.5891	.6347	.6804	.7260	.7717	.8174	.8630	.9084	.9543
5.0	.....	.5410	.5869	.6328	.6787	.7246	.7705	.8164	.8623	.9082	.9541

Fig. 3.

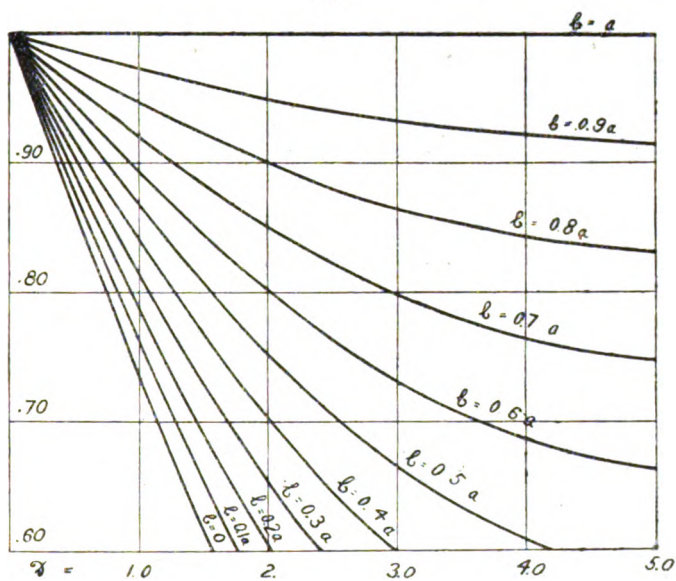


Fig. 4.

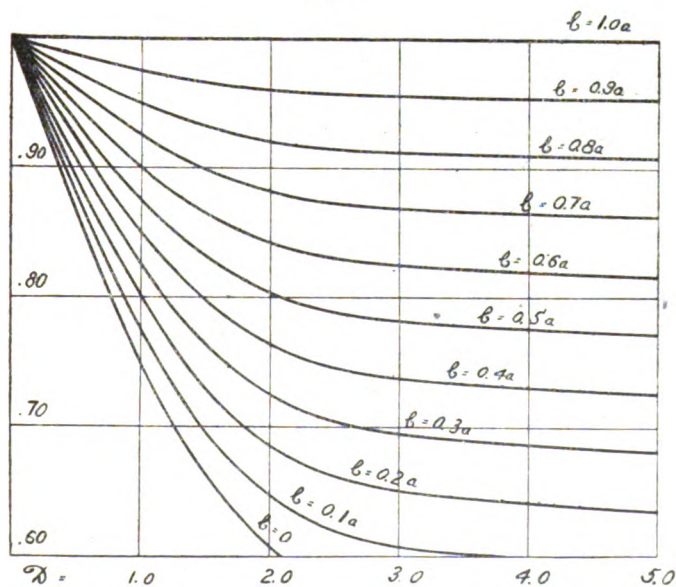


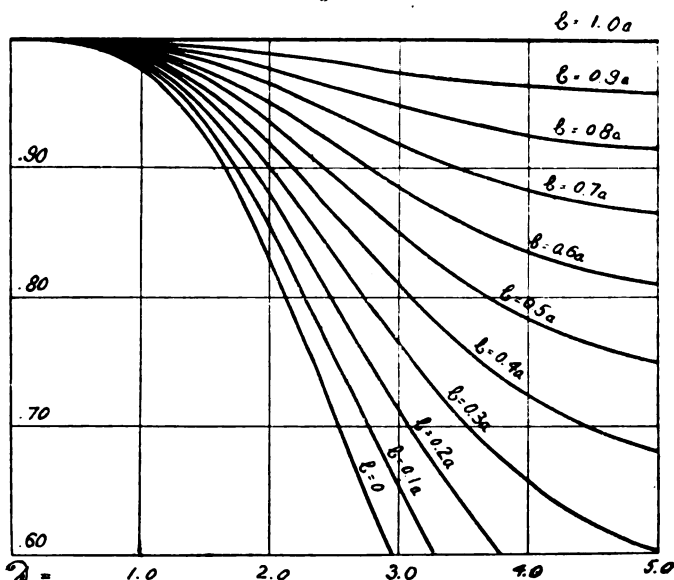


TABLE III.

D.	b = 0.	0.1.	0.2.	0.3.	0.4.	0.5.	0.6.	0.7.	0.8.	0.9.
0.1	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
0.2	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
0.4	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
0.6	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
0.8	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
1.0	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
1.2	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
1.4	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
1.6	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
1.8	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
2.0	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
2.2	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
2.4	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
2.6	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
2.8	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
3.0	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
3.2	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
3.4	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
3.6	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
3.8	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
4.0	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
4.2	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
4.4	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
4.6	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
4.8	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
5.0	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000

In the case of  $b > 0$ , *i. e.*, when the band has some brightness, the latter is expressed in terms of  $a$ —brightness of the planes being assumed to be equal to unity. The values of illumination at the axis and that at the edges are given in the Tables I. and II., and for some values of  $D$  and  $b$  in figs. 3 and 4.

Fig. 5.



We see that the illuminations at the axis for small values of  $D$  do not differ much the one from the other with increasing  $b$ , but with increasing  $D$  the difference of illumination at the axis for different  $b$  increases rapidly. The curves of fig. 3 representing the illumination at the axis for different  $D$  and  $b$  approach asymptotically the value of  $b$ . As  $b$  increases the value of  $D$ , for which the illumination at the axis differs but very little from  $b$ , decreases rapidly; for example, for  $D=5.0$  and  $b=0.9$  the illumination is about 0.91.

The illuminations at the geometrical images of the edges, as shown in the Table II. and fig. 4, differ more and more with increasing  $D$  ( $b$  being constant) and with decreasing  $b$  ( $D$  being constant).

If  $b > a$ , say  $b = 1.10, 1.20, 1.30$ , etc., the curves in figs. 3

and 4 will be symmetrical with the curves for  $b=0.9, 0.8, 0.7$ , etc., with respect to the line  $b=1.0$ .

The diffraction conditions of visibility of a band of width  $D$  and brightness  $b$  on a background of brightness  $a$  seen by means of an object-glass depend on the contrast between the illumination at the axis of a band and that of the background in their diffraction image and on the contrast sensibility of the eye. The latter has been determined in different ways and by several authors, but only for two adjacent fields. As the limit of contrast sensibility of the eye we can admit 2 per cent. for the most favourable conditions of brightness of the fields. For a diffraction image of a band on a bright background the case of adjacent fields cannot be applied. We have no experimental determination of contrast sensibility of the eye for the case when the illumination of field has some minimum with slow or rapid increasing to general illumination.

Michelson\* has investigated this case theoretically for an object-glass with a rectangular aperture and found that a dark line on a bright background is still visible when its width is 50 times less than the limit of resolution for two fine lines, the latter being admitted equal to  $\pi$  (Lord Rayleigh criterium). Michelson in his considerations used as limit of contrast sensibility of the eye 2 per cent., but for the distance  $=\pi$ , the percentage difference of illumination at maximum and at central minimum in a diffraction image of two fine lines is equal to about 20 per cent. (Rayleigh), so even if the conditions of visibility of a band of width  $D$  and the conditions of resolution of two fine lines at distance  $D$  may be considered identical, the band of width  $D$  is visible only 5 times easier than two lines resolved.

If we call critical distance the distance between two planes or the width of a *dark* band between them, for which the percentage difference of illumination at the axis of a band and that at a sufficient distance from it in their diffraction image is equal to zero, the critical distance is equal to zero. (For two luminous points of equal brightness the critical distance will be that for which the percentage difference of illumination at maximum, at or near the geometrical image of one point, and that at central minimum is equal to zero; it is equal to  $D=3.0$ .)

If we assume as limit of contrast sensibility of the eye 5, 10, 15, 20 per cent. two planes must be at the following distances for different values of  $b$ , so as to be resolved by the eye.

\* Astrophysical Journal, ii. p. 60 (1895).

TABLE IV.

$b$ .	5.	10.	15.	20.
0	0.17	0.37	0.55	0.73
0.1	0.18	0.41	0.62	0.83
0.2	0.23	0.45	0.72	0.95
0.3	0.26	0.53	0.80	1.08
0.4	0.27	0.61	0.96	1.28
0.5	0.38	0.75	1.14	1.56
0.6	0.47	0.94	1.46	2.04
0.7	0.62	1.30	2.01	2.97
0.8	0.94	2.01	3.60	—
0.9	2.14	—	—	—

These distances expressed as  $D$  may be easily converted into angular distances by means of (18). For comparison I give here the corresponding distances for two luminous points of equal brightness on a dark background from my paper "Diffraction Pattern in a case of two very close Point-Light Sources" \* :

5.	10.	15.	20.
3.28	3.43	3.56	3.68

If we admit, *rather arbitrarily*, the limit of contrast sensibility of the eye for the case of diffraction image of two planes with a band between them to be 10–15 per cent., we shall have that two planes with a dark band between them ( $b=0$ ) are resolved 9–6 times easier than two points, if generally the conditions of resolution of two planes and two points may be considered identical. For  $b>0$  the distances between two planes to be resolved must be greater (see Table IV.). When  $a-b$  is less than the assumed limit value of contrast sensibility of the eye, two planes cannot be resolved (see the last line of Table IV.).

A diffraction image of two luminous planes with a dark band or a band of some brightness between them may serve as a convenient object for determining the contrast sensibility of the eye, as we can vary the contrasts within large limits, their calculation is very simple and generally the distribution of illumination in such a diffraction image is clearly definite as all the isophotes are straight lines.

The author is much indebted to Mr. G. Wahrlich for the execution of the drawings.

\* Phil. Mag. xlv. p. 29 (1923).

XC. *Note on the Striking Potential necessary to produce a Persistent Arc in Vacuum.* By F. SIMEON, B.Sc., F.Inst.P., Physicist in the Research Laboratories of Adam Hilger, Ltd.\*

THE ease with which an arc can be struck in air between two electrodes of carbon or of such a metal as copper and the convenience of such an arc as a light source in spectroscopy, have suggested to those who have experimented in vacuum spectroscopy that an arc *in vacuo* would be convenient and desirable in that region also. When tried, however, it is found that with a number of substances the arc is intermittent when the voltage available for striking is of the order of 100–200 volts. In addition, it is well known that arcs *in vacuo* emit radiations corresponding to the spark lines of the element in question.

In the course of some experiments on the spectrum of carbon in vacuum, its appearance was noted when the applied voltage had several values. For 40 volts or more the arc was as persistent as in air, but the distance between the electrodes could not be made so great, this distance depending upon the voltage and the time the arc had been running (*i. e.*, probably on the temperature of the electrodes). When the striking potential was reduced to 30 volts, the arc would no longer persist, a momentary flash only being produced when the electrodes were slightly separated after being touched together, the appearance being similar to that obtained with two copper electrodes for a striking potential of 220 volts. A marked change in the spectrum of the arc occurred simultaneously with the change in appearance. A striking potential of 40 volts was sufficient to excite the complete spectrum as given by 220 volts, including the lines near 385 Å, identified by Millikan† as the  $L\alpha$  lines of carbon; but with 30 volts the  $L\alpha$  and some associated lines were suppressed, still leaving, however, a number of recognized spark lines—*e. g.*, 2297, 2509, and 2512 Å. This shows that the lower potential is sufficient to ionize carbon atoms by removal of one of the outer electrons, but insufficient to excite radiation corresponding to the L levels.

To test whether there is a connexion between L radiation and the persistence of the arc *in vacuo*, arcs were formed

\* Communicated by Prof. A. W. Porter, D.Sc., F.R.S.

† Millikan, *Astrophys. Journ.* lii. pp. 47–64 (July 1920).

with the elements Cu, Al, Si, and Na. The results are:—

Element.	Observed voltage.		Calculated voltage.
	More than.	Less than.	
Cu .....	220	—	950
Al .....	80	100	87
Si .....	95	105	100
Na .....	30	40	34

The second column gives the limits within which the voltage corresponding to the beginning of persistence could be decided on. Means were not to hand for obtaining direct current at about 1000 volts, so that in the case of copper the probable value could not be approached, and only a transitory flash could be obtained on touching the electrodes together and separating them. The limits given for aluminium are wider than for the remaining two elements because of the “sticky” nature of the arc, the electrodes appearing to fuse together at the point of contact, so that the effort to separate them often caused the arc to be made longer than could be maintained.

The numbers given in the third column of the table are obtained from the quantum relation

$$Ve = h\nu,$$

the value assigned to  $\nu$  being that corresponding to the L lines of the element in question. Siegbahn’s\* value of wave-length 13·309 Å. was used for copper, and Millikan’s† value 372 Å. for sodium. The approximate values for aluminium and silicon were obtained by means of Kossel’s Combination Principle,

$$L\alpha = K\beta - K\alpha.$$

A check value for aluminium was obtained by taking Millikan’s line at 136 Å. as the limit for this metal, the corresponding voltage being 92.

It is interesting to compare these results in one or two instances with corresponding results for an arc in air at ordinary pressures. An immense amount of work has been done on the carbon arc, and various formulæ given connecting the applied voltage and the length of the arc. Fröhlich‡ established the linear relation

$$V = m + nl,$$

in which  $m$  and  $n$  are constants. Von Lang has determined

\* Siegbahn, *Jarhb. d. Rad.* xviii. (3) pp. 240-292 (1921).

† Millikan, *Nat. Acad. Sci. Proc.* (Oct. 1921).

‡ Fröhlich, *Elektrotechnische Zeitschrift*, iv. p. 150 (1883).

the value  $m=35$  volts for carbon. More recently Steinmetz\* has given the formula

$$V = V_0 + a \frac{(l+b)}{\sqrt{i}},$$

in which  $i$  is the current and  $V_0$ ,  $a$  and  $b$  constants. For carbon he gives  $V_0=36$  volts. In this case, therefore, there is good agreement with the vacuum value for carbon ( $>30 <40$ ) and with that given by the quantum relation for the limit of the carbon spectrum as determined by Millikan † at 360 Å., viz. 35 volts.

In the case of copper the evidence is conflicting. Von Lang has determined  $m$  in Fröhlich's formula as 23·86 volts, while Arons ‡ has found the potential difference required to produce an arc 1·5 mm. long carrying a current of 4·5 amperes to be 27 volts in air and 30 volts in pure nitrogen. The low value given by v. Lang is probably explained as being a constant found by extrapolation upon plotting results obtained with arcs of various lengths which had been established sufficiently long to have a plentiful supply of electrons of thermionic origin. The value thus obtained would represent the voltage required to maintain an arc of zero length which had already been formed. It seemed best in this case to observe the appearance of the flash produced when two clean copper electrodes were touched together in air. For a potential difference of 10 volts a small spark was produced which did not have the characteristic green colour of the copper arc, which colour did not appear until about 25 volts difference of potential was attained. When the difference had increased to 30 volts, the arc would almost persist, and did persist at 35 volts. Identical observations were made in the case of aluminium, although for this metal Arons gives the values 39 volts for air and 27 for nitrogen.

It is at least clear from these results of v. Lang and Arons that the potential difference required to initiate a persistent arc in air is not determined by the excitation of the L-series corresponding to the electrodes, but is almost, if not quite, a constant quantity. It would therefore seem that in air the nature of the electrodes is not of importance as regards the voltage required to establish an arc, but that this depends chiefly upon the atmosphere in which it is formed.

\* Steinmetz, cf. Pidduck's 'Electricity,' p. 361 (Camb. Univ. Press, 1916).

† Millikan, *Astrophys. Journ.* lii. pp. 47-64 (July 1920).

‡ Arons, *Ann. der Phys.* i. p. 700 (1900).

But it does not seem to be necessary in this case to excite the L-series of the gases in the atmosphere, for the highest value given (*i. e.* Arons' value for aluminium in air) is less than the expected value for nitrogen, and still less than that for oxygen. For the latter gas the limit of the L-series is placed at 248 Å. by Kurth\* and at 231 Å. by Millikan†, which correspond to voltages of about 50–55. For nitrogen the corresponding value will be intermediate between this and carbon, and will be expected nearer to the former in view of Mohler and Foote's‡ values for the K series.

It is to be noticed that no suggestion is made regarding the carriers of current in a fully-established arc, a full discussion of which has been given recently by Compton§; but if his views receive acceptance, the above considerations may suggest the origin of the positive ions whose presence gives the positive space-charge which enables sufficient electrons to be present to carry the currents observed in practice.

*XCI. The Two-Dimensional Motion of a Lamina in a Resisting Medium under the Action of a Propeller Thrust.*  
By S. LISTER, M.Sc. ||

THE "phugoids," or "flight curves," of a lamina moving in a resisting medium under no external forces other than its own weight, have been investigated by F. W. Lanchester¶ and S. Brodetsky\*\*. The object of this paper is to extend the investigation by the introduction of a propeller thrust.

Under Lanchester's assumptions the body has a vanishingly small moment of inertia, the velocity has a direction fixed in the body, and there is no loss of energy. The lamina thus maintains the same mean level throughout the motion.

The assumptions made in this paper are, however, those used by Brodetsky, viz., a large moment of inertia, as in the case of a lamina attached to a heavy engine. Small changes in angular velocity can then be neglected and the lamina rotates with uniform angular velocity,  $\omega$ .

\* Kurth, Phys. Rev. xviii. pp. 461–476 (1921).

† Millikan, Nat. Acad. Sci. Proc. (Oct. 1921).

‡ Mohler & Foote, Phys. Rev. xix. pp. 434–435 (1922).

§ Compton, Phys. Rev. xxi. (3) pp. 266–291 (March 1923).

|| Communicated by the Author.

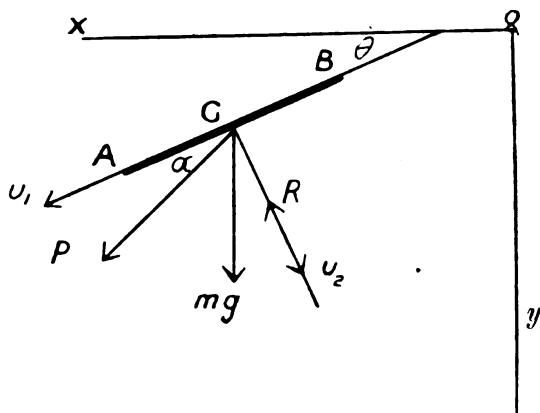
¶ Lanchester, 'Aerodionetics.' Constable, pp. 37–65.

\*\* Brodetsky, Proc. Roy. Soc. A. vol. xcv. pp. 516–532 (1919);  
'Mechanical Principles of the Aeroplane.' Churchill, pp. 87–93.



The resistance,  $R$ , of the medium is assumed to be perpendicular to the lamina, and to pass through  $G$ , the centre of gravity.

Fig. 1.



The propeller thrust,  $P$ , is inclined at an angle  $\alpha$  to the lamina.

The velocities of the lamina along and perpendicular to  $BA$  are  $u_1$  and  $u_2$ .

I. *Resistance Proportional to the Velocity*:  $R = m\kappa u_2$ .

(a) *Constant Propeller Thrust applied along the Lamina*:  $P = m\lambda$ ,  $\alpha = 0$ ,  $R = m\kappa u_2$ ,  $\lambda$  and  $\kappa$  being constants.

The equations of motion are :

$$\left. \begin{aligned} \frac{du_1}{dt} - u_2 \frac{d\theta}{dt} &= g \sin \theta + \lambda, \\ \frac{du_2}{dt} + u_1 \frac{d\theta}{dt} &= g \cos \theta - \kappa u_2, \\ \frac{d^2\theta}{dt^2} &= 0. \end{aligned} \right\} \dots \dots (1)$$

Hence  $\dot{\theta} = \omega$ ; changing the independent variable to  $\theta$ , and eliminating  $u_2$ , we get

$$\frac{d^2 u_1}{d\theta^2} + \frac{\kappa}{\omega} \frac{du_1}{d\theta} + u_1 = \frac{2g}{\omega} \cos \theta + \frac{\kappa g}{\omega^2} \sin \theta + \frac{\kappa \lambda}{\omega^2}.$$

The complementary function has a factor  $e^{-\frac{\kappa\theta}{2\omega}}$ , and ceases

to be of importance after a time. The particular integral is

$$u_1 = -\frac{g}{\omega} \cos \theta + \frac{2g}{\kappa} \sin \theta + \frac{\kappa \lambda}{\omega^2}, \quad \left. \begin{array}{l} \text{and hence, } u_2 = \frac{2g}{\kappa} \cos \theta \\ \qquad \qquad \qquad -\frac{\lambda}{\omega}. \end{array} \right\} \dots (2)$$

If the time be measured from an instant when  $\theta=0$ ,  $\theta=\omega t$ . It is now evident from these equations that the motion is periodic, with period  $\frac{2\pi}{\omega}$ .

The equations of the flight curve, *i. e.*, the path of the centre of gravity, can now be obtained in terms of the parameter  $\theta$ , since

$$\frac{dx}{dt} = u_1 \cos \theta - u_2 \sin \theta, \quad \text{and} \quad \frac{dy}{dt} = u_1 \sin \theta + u_2 \cos \theta.$$

Substituting, integrating, and choosing the origin so that the terms independent of  $t$  vanish, we get

$$\left. \begin{array}{l} x = -\frac{gt}{2\omega} - \frac{g}{4\omega^2} \sin 2\omega t + \frac{\lambda}{\omega^2} \left( \frac{\kappa}{\omega} \sin \omega t - \cos \omega t \right), \\ \text{and} \\ y = \frac{2gt}{\kappa} + \frac{g}{4\omega^2} \cos 2\omega t - \frac{\lambda}{\omega^2} \left( \frac{\kappa}{\omega} \cos \omega t + \sin \omega t \right). \end{array} \right\} \dots (3)$$

By an alteration in the scales in the ratio  $1 : \frac{4\omega^2}{g}$ , these equations may be written

$$\left. \begin{array}{l} x = -2\theta - \sin 2\theta + 4 \cdot \frac{\lambda}{g} \left( \frac{\kappa}{\omega} \sin \theta - \cos \theta \right), \\ y = \frac{4\omega}{\kappa} \cdot 2\theta + \cos 2\theta - 4 \cdot \frac{\lambda}{g} \left( \frac{\kappa}{\omega} \cos \theta + \sin \theta \right). \end{array} \right\}$$

It will be seen from these equations that the flight curves are trochoidal in form and represent a general fall along the line  $y = -\frac{4\omega}{\kappa} \cdot x$ , the mean rate of fall being  $\frac{2g}{\kappa}$  for all values of  $\lambda$ , including the case of no propeller thrust, ( $\lambda=0$ ).

When  $\lambda=0$ , the flight curves can, by turning the axes and changing the origin and parameter, be put in the form

$$\left. \begin{array}{l} x = \phi \sec \beta + \sin \phi, \\ y = \sec \beta - \cos \phi, \end{array} \right\}$$

where  $\tan \beta = \frac{4\omega}{\kappa}$ , and  $\phi = 2\theta + \beta$ .

The flight curves for no propeller thrust are therefore pure trochoids, without loops or cusps\*. The propeller thrust, however, introduces both loops and cusps into the flight curves.

The lamina cannot reproduce its initial motion for any value of the propeller thrust, and hence it can never describe a closed path. There is, in fact, a loss of energy equal in amount to  $\int(\kappa u_2^2 - \lambda u_1)dt$  per unit mass, and if the integration be taken over a period, we get  $\frac{4\pi g^2}{\kappa\omega}$  for all values of  $\lambda$ . It will be noticed also that, for a given value of  $\omega$ , the greater the value of  $\kappa$ , the more nearly does the mean path approximate to the horizontal, and the smaller is the loss of energy. Also, the mean rate of fall is just twice as great as if the lamina were to fall as a parachute, and is independent of the rotation†.

*Cusps.* The cusps are of interest, representing, as they do, the extreme case of "stalling," or loss of flying speed. They occur when the resultant velocity becomes zero and changes its direction through  $180^\circ$ , i.e. when the  $u_1$ ,  $u_2$  curves pass through the origin. Hence, for cusps, we have

$$\text{and} \quad \left. \begin{aligned} -\frac{g}{\omega} \cos \theta + \frac{2g}{\kappa} \sin \theta + \frac{\kappa\lambda}{\omega^2} &= 0, \\ \frac{2g}{\kappa} \cos \theta - \frac{\lambda}{\omega} &= 0, \end{aligned} \right\}$$

whence

$$\text{and} \quad \left. \begin{aligned} \tan \theta &= -\frac{\kappa}{2\omega}, \\ \lambda &= \frac{2\omega}{\kappa} \cos \theta = \frac{4\omega^2}{\kappa^2} \left(1 + \frac{4\omega^2}{\kappa^2}\right)^{-1/2} \end{aligned} \right\} \quad \dots \quad (4)$$

*Loops.* For greater values of  $\frac{\lambda}{g}$ , the cusps develop into loops, and the characteristic features of looping present themselves, viz., the dive to gain speed, the summit of the loop being reached in an upside-down position, and the dive again to regain normal flying speed.

\* Edwards, 'Differential Calculus,' p. 343.

† Brodetsky, *loc. cit.*

(b) *Propeller Thrust Inclined at an Angle  $\alpha$  to the Lamina.*

The equations of motion are :—

$$\left. \begin{aligned} \frac{du_1}{dt} - u_2 \frac{d\theta}{dt} &= g \sin \theta + \lambda \cos \alpha, \\ \frac{du_2}{dt} + u_1 \frac{d\theta}{dt} &= g \cos \theta - \kappa u_2 + \lambda \sin \alpha, \\ \frac{d^2\theta}{dt^2} &= 0. \end{aligned} \right\} \quad . \quad (5)$$

Proceeding as in I(a), we get

$$\left. \begin{aligned} x &= -\frac{gt}{2\omega} - \frac{g}{4\omega^2} \sin 2\omega t + \frac{\lambda}{\omega^2} \left( \frac{\kappa}{\omega} \cos \alpha + \sin \alpha \right) \sin \omega t \\ &\quad - \frac{\lambda}{\omega^2} \cos \alpha \cos \omega t, \\ y &= \frac{2gt}{\kappa} + \frac{g}{4\omega^2} \cos 2\omega t - \frac{\lambda}{\omega^2} \left( \frac{\kappa}{\omega} \cos \alpha + \sin \alpha \right) \cos \omega t \\ &\quad - \frac{\lambda}{\omega^2} \cos \alpha \sin \omega t. \end{aligned} \right\}$$

Comparing these with equations (3), and writing  $\lambda', \kappa', \omega', g'$ , for the values which must be given to  $\lambda, \kappa, \omega, g$  in the previous case to obtain the above equations, we have the following substitutions :—

$$\omega' = \omega, \quad g' = g, \quad \lambda' = \lambda \cos \alpha, \quad \kappa' = \kappa + \omega \tan \alpha.$$

The case when  $\alpha \neq 0$  is thus reduced to a simple application of that when  $\alpha = 0$ .

(c) Other cases have been worked out in which attempts were made to allow for the decreasing efficiency of the propeller at higher speeds, *e.g.*, the propeller thrust was assumed to diminish exponentially as the speed of the lamina increased. The manipulation became rather heavy and it is omitted here; the flight curves obtained showed the same characteristic features as those obtained in the preceding cases.

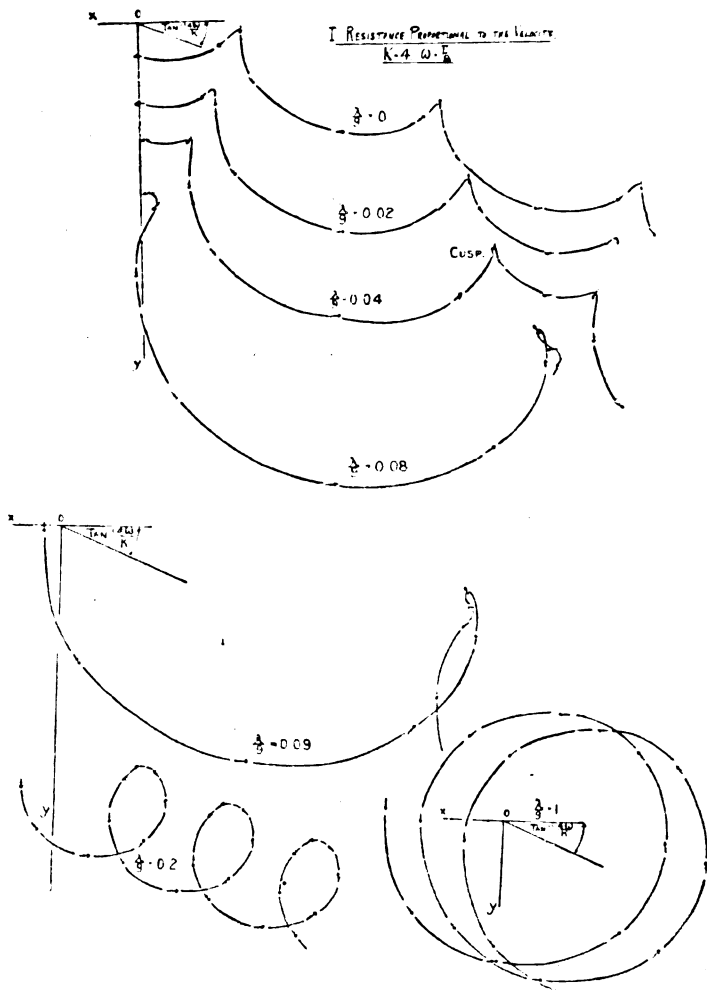
### *The Flight Curves.*

For the most part these were drawn by direct computation from the equations, but in more complicated cases they were obtained by plotting  $u_1$  against  $u_2$  and marking the time intervals on the velocity curves thus obtained. The resultant velocity was easily obtained from the  $u_1, u_2$  curves

from instant to instant, and thence the flight curves were drawn.

In the diagrams shown, the same values of  $\kappa$  and  $\omega$  are

Fig. 2.



used, so that the mean line of descent is the same for all the flight curves. They aim at showing how the curves change as the propeller thrust is increased.

For zero propeller thrust, the curves are pure trochoids without loops or cusps. For small values of the propeller

thrust, the flight curves have two unequal undulations per period. As the propeller thrust is increased, the smaller undulation decreases in size and the transition crest becomes sharper and sharper, until, finally, it becomes a cusp. On further increasing the propeller thrust, the smaller undulation develops a loop, the loop growing in size until, for values of  $\frac{\lambda}{g}$  approaching unity (a very extreme case in practice), the flight curves assume the appearance of a "travelling circle."

## II. Resistance Proportional to the Square of the Velocity.

Let the resultant velocity,  $V$ , make an angle,  $\gamma$ , with the lamina. Neglecting, for the present, all external forces except the resistance of the medium, and assuming  $R = AV^2 \sin \gamma$ , where  $A$  is a constant, we get as the equations of motion:—

$$\left. \begin{aligned} \frac{du_1}{dt} - u_2 \frac{d\theta}{dt} &= 0, \\ \frac{du_2}{dt} + u_1 \frac{d\theta}{dt} &= -AV^2 \sin \gamma, \\ \frac{d^2\theta}{dt^2} &= 0. \end{aligned} \right\} \dots \dots (6)$$

These reduce to

$$\left. \begin{aligned} \frac{du_1}{dt} &= \omega u_2, \\ \frac{du_2}{dt} + \omega u_1 + Au_2 V &= 0, \\ \dot{\theta} &= \omega; \end{aligned} \right\}$$

and again to

$$\frac{dV}{du_1} = -ku_2, \text{ where } k = \frac{A}{\omega}.$$

This equation does not appear to be integrable in exact terms, and Brodetsky's graphical method of solution is adopted\*.  $k$  only affects the scale of the curves, and, if the

\* Mathematical Gazette, vols. ix. & x., nos. 142, 144-6; and Piaggio, 'Differential Equations,' pp. 5-9.

$u_1, u_2$  curves be drawn from the equation

$$\frac{dV}{du_1} = -u_2 \dots \dots \dots (7)$$

the radius vector must be multiplied by  $1/k$  to obtain the correct value of  $V^*$ .

Also, following a suggestion by Prof. L. J. Rogers, the orthogonal trajectories of (7) are easily found.

Since  $V^2 = u_1^2 + u_2^2$ , we have for the orthogonal trajectories

$$\frac{du_1}{du_2} = \frac{u_1}{u_2} + V.$$

Putting  $u_1 = z \cdot u_2$ , we get

$$\frac{dz}{du_2} = (1 + z^2)^{1/2},$$

whence

$$u_1 = u_2 \sinh(u_2 + B),$$

$B$  being an arbitrary constant.

Remembering the change of sign on passing through the lamina, the orthogonal trajectories can be plotted, and the solution of (6) obtained in graphical form.

The corrections for the propeller thrust and the weight were then applied and the final  $u_1, u_2$  curves were obtained for  $\frac{1}{4}$ -second time intervals. Some of the flight curves are given, but the graphical solution of (7) and the velocity curves are omitted.

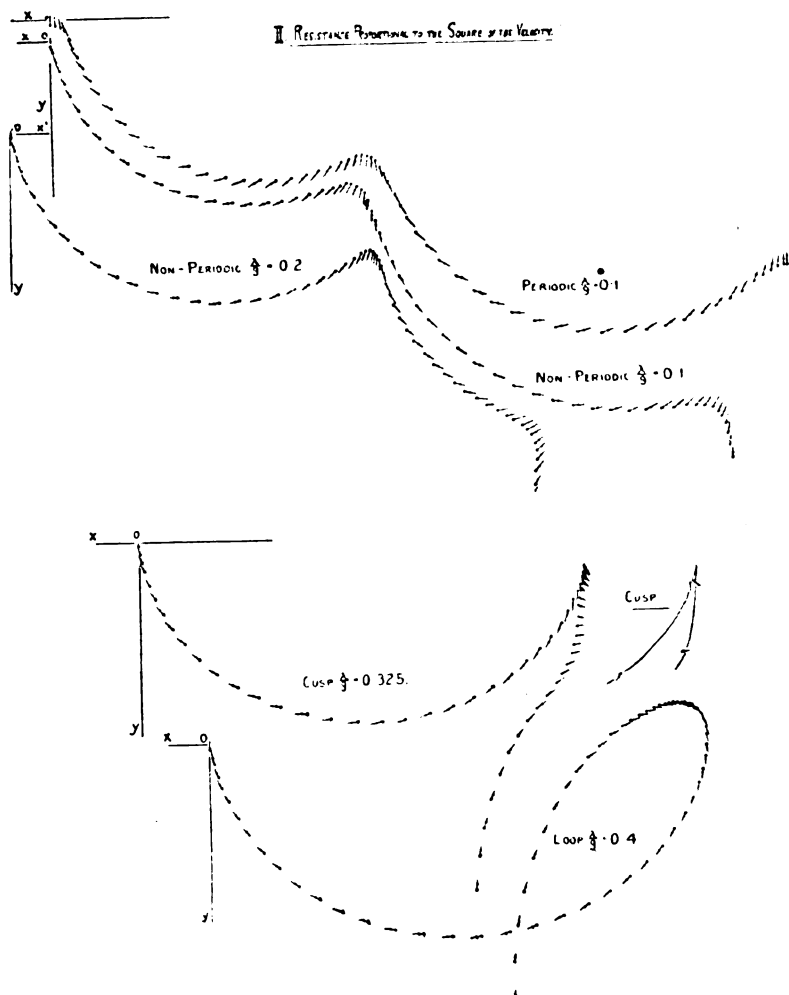
### *Flight Curves.*

It will be noticed that the curves are not in general periodic. To obtain periodic curves it is necessary to obtain  $u_1, u_2$  curves which form a closed path. Cusps are obtained by finding  $u_1, u_2$  curves which pass through the origin. The velocity curves for periodic motion and cusps are obtained by a process of trial and error. Attempts to find a periodic curve with a cusp proved unsuccessful.

It will be seen from the diagrams that the general features, except that of periodicity, are much the same as in the case of the resistance varying as the first power of the velocity, the increase in the propeller force producing the same series of changes as before.

\* This analysis is taken from Brodetsky's paper, already referred to above.

Fig. 3.



In conclusion, I desire to express my indebtedness to Dr. S. Brodetsky for suggesting this work, and for his very valuable advice and criticism throughout the investigation.



XVII. *Ionizing Potentials of Helium and some Multiatomic Gases.* By C. A. MACKAY, M.A., 1851 Exhibition Fellow, Princeton University\*.

THE study of radiating and ionizing potentials of metallic vapours and monatomic gases has been of great importance in developing the theory of line spectra and atomic structure. In the case of multiatomic gases, the conditions are more complicated, and relatively little progress has been made either in the direction of obtaining comprehensive and reliable experimental data or of relating these data to spectroscopic, chemical, or other properties of the molecules and their constituent atoms. Reviews of the experimental and theoretical aspects of these problems are given by Hughes† and by Foote and Mohler‡.

Born§ and Fajans|| have calculated the ionizing potentials of HCl, HBr, and HI. These have been measured by Knipping,¶ who gives values close to those predicted. Foote and Mohler\*\* also calculated the ionizing potentials to be expected for the case of certain compound gases in which the process of ionization may reasonably be assumed to take the form of splitting up the molecule into positively and negatively charged atoms for which there are sufficient thermochemical data to predict the ionizing potentials. Beyond the metallic vapours—hydrogen, helium, and a few compounds—no ionizing potentials have been calculated, but some correlations have been suggested by Smyth†† and Foote and Mohler‡‡ between the radiating potentials they found and the lines in the spectrum of nitrogen.

In view of this situation, it was considered of importance to investigate as large a number of related multiatomic gases as possible, to serve as a basis of further theoretical developments. The present paper presents the results thus far obtained in an investigation which is to be extended to other gases.

The method employed was suggested by Hughes and

\* Communicated by Professor K. T. Compton.

† Bull. Nat. Research Council, vol. ii. pt. 2, No. 10.

‡ 'Origin of Spectra'

§ *V. d. D. P. G.* vol. xxi. p. 13 (1917).

|| *V. d. D. P. G.* vol. xxi. p. 714 (1919).

¶ *Zeit. f. Phys.* vol. vii. p. 328 (1921); also Franck, *Zeit. f. Phys.* vol. xi. p. 160 (1922).

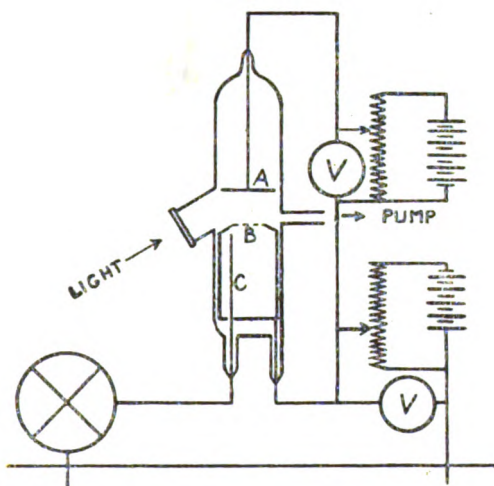
\*\* Journ. Wash. Acad. Sci. vol. x. p. 435 (1920).

†† Phys. Rev. vol. xiv. p. 409 (1919).

‡‡ J. O. S. A. vol. iv. p. 49 (1920).

Dixon \*, though it was not the one they finally adopted in their work. A nickel target (A, fig. 1) illuminated by ultra-violet light from a quartz-mercury arc lamp provided a source of electrons. This arrangement had two advantages over a hot filament; it did not decompose the compound gases, and it was not attacked by gases such as oxygen and water vapour. The electrons were accelerated towards the platinum gauze B by means of a variable electric field. Between B and the electrode C a constant difference of potential was maintained in such a direction that positive ions would be attracted to C. In order that a minimum

Fig. 1.



amount of any radiation, emitted by the molecules on electron impact, should fall on C, it was made of a fine platinum wire with extremely small area. As a consequence, the amount of photo-electric effect produced in C was negligible, and thus the apparatus was rendered insensitive to radiation effects. On the other hand, the wire was effective as a collector of ions. The rate at which C became charged was measured by a Compton electrometer with a sensitivity of approximately 2000 mmr. deflexion per volt.

The electrons emitted from the surface of the nickel target had kinetic energy varying from zero to that corresponding to about two volts. The distribution of the velocities of the electrons depended on the character of the light from the

\* Phys. Rev. vol. x. p. 495 (1917).

arc lamp, though even if it had been strictly monochromatic, the velocities would not have been uniform. Ionization began as soon as the fastest electrons had kinetic energy equivalent to the ionizing potential, and this energy was the sum of the initial energy of the electrons at the surface of the target together with the energy resulting from the electric field between A and B. Some means had to be found to take into consideration the former energy so that the applied difference of potential plus a correction would give the actual energy of the electrons producing ionization. Several methods which have been used in other work are discussed by Smyth\*. They are usually based on some theoretical or experimental curve which shows the velocity distribution of the electrons after they have been accelerated by the applied electric field. In a later paper Brandt † gives a more direct method, which is satisfactory provided the ionizing potential of one substance, which is used as a standard, is accurately known by some independent means. The principal series of the mercury spectrum has a convergence limit corresponding to an ionizing potential of  $10\cdot392\frac{1}{2}$ ; so that mercury was chosen as the standard. If helium is mixed with mercury vapour and the ionizing potentials of both substances are measured, then the difference between the potentials will be the same for any distribution of velocities of electrons used in actual measurements. Neither will corrections due to contact difference of potential between the nickel and platinum electrodes need to be applied, nor will surface effects such as found by Brandt and assumed to be produced by layers of polarized molecules of the gas be a disturbing factor. Let us suppose that the observed values for mercury and helium are  $10\cdot2$  and  $24\cdot3$  volts. The correction for mercury is evidently  $\cdot2$  volt (if  $10\cdot4$  is taken as the correct value), and accordingly to keep the difference between the ionizing potentials the same,  $\cdot2$  volt must be added to the helium value, making the corrected result  $24\cdot5$  volts. Helium was chosen because its high radiating and ionizing potentials would prevent confusion with the critical potentials of any other gases, and its chemical inertness would prevent combination with other gases to be mixed with it. Brandt found that nitrogen, having a lower radiating potential than helium, was unsatisfactory. Having thus obtained the corrected value for helium, it was mixed with another gas and the difference in the ionizing potentials

\* Phys. Rev. vol. v. p. 14 (1919).

† *Zeit. f. Phys.* vol. viii. p. 32 (Dec. 1921).

‡ Foote and Mohler, 'Origin of Spectra,' p. 64.

was measured. The difference was subtracted from the corrected value of the ionizing potential of helium, and the result was taken as the corrected value of the ionizing potential of the gas. The corrections varied from  $\cdot 1$  to  $\cdot 5$  volt in different gases.

To insure that adsorbed gases from the glass were removed, the whole apparatus was exhausted by means of a Langmuir diffusion pump until a McLeod gauge showed no trace of pressure. It was then allowed to stand for 24 hours and re-exhausted. After another equal interval, the experimental tube was "washed out" several times with the gas that was being measured. Either phosphorus-pentoxide or soda-lime tubes were used for drying, and mercury vapour was removed by two traps surrounded by liquid air or carbon-dioxide snow mixed with alcohol. It was found that traces of impurities could be easily detected by a comparison of the curves obtained when they were present with the curves of the pure gas. The most convenient pressures were determined by a few preliminary trials. They varied with different gases, but were all within the limits  $\cdot 001$  mm. and  $\cdot 05$  mm. of mercury.

Since the helium was used repeatedly, an apparatus was set up to recover and repurify it after every run. This consisted of a Geissler-Toepler pump connected with a small drying-tube and a charcoal trap, so arranged that the helium could be pumped out of the experimental tube and then forced through the trap, which was immersed in liquid air. The gas was stored in the drying-tube. The curves plotted from data for helium showed that the impurities were completely removed by repeated pumping through the charcoal.

The other gases were made by the usual chemical procedure from pure reagents. In the work with water vapour it was found that a convenient vapour-pressure could be obtained if potassium hydroxide was allowed to come to equilibrium with its vapour-pressure at room temperature. Since hydrogen iodide attacks mercury, so that it could not be pumped through the Langmuir pump, the gas was admitted at a pressure rather higher than desired, and the excess was taken up by a tube of fused potassium hydroxide.

Readings were not taken until thirty minutes after the target had been illuminated to permit the emission of electrons to become nearly constant. The retarding field between B and C which gave the most satisfactory results was between  $6\cdot 0$  and  $8\cdot 0$  volts. The accelerating field from A to B was varied by steps of  $\cdot 1$  or  $\cdot 2$  volt over a range from 0 to 50 volts, with an accuracy of the voltage readings

better than  $\cdot 05$  volt. The electrometer deflexions were timed by a stop-watch graduated to  $\cdot 1$  second with a probable error less than  $\cdot 05$  second. A series of wire screens in front of the lamp were arranged to regulate the intensity of the ultra-violet light so that no reading of less than

Fig. 2.

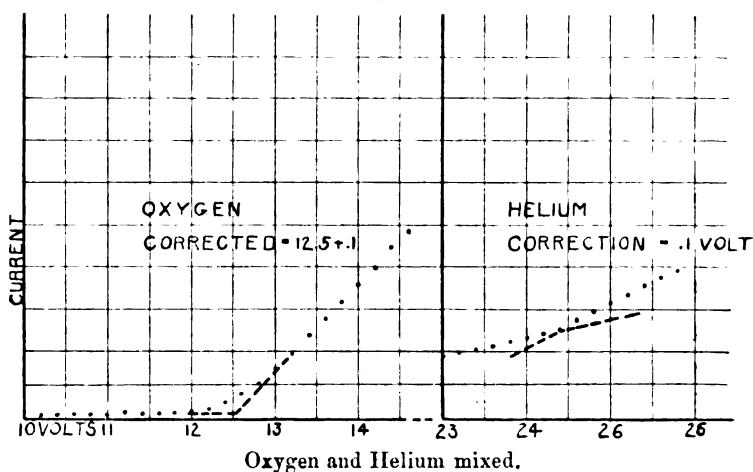
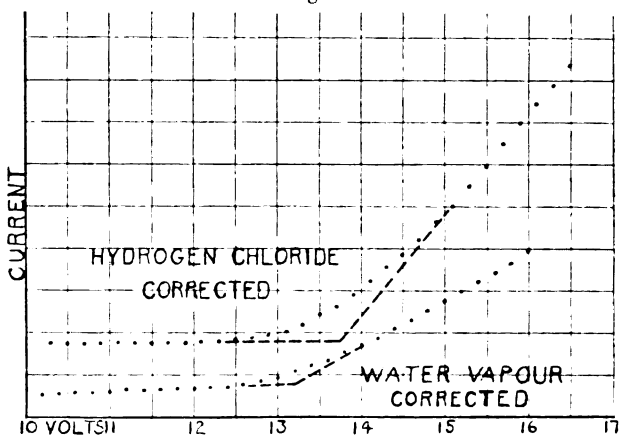


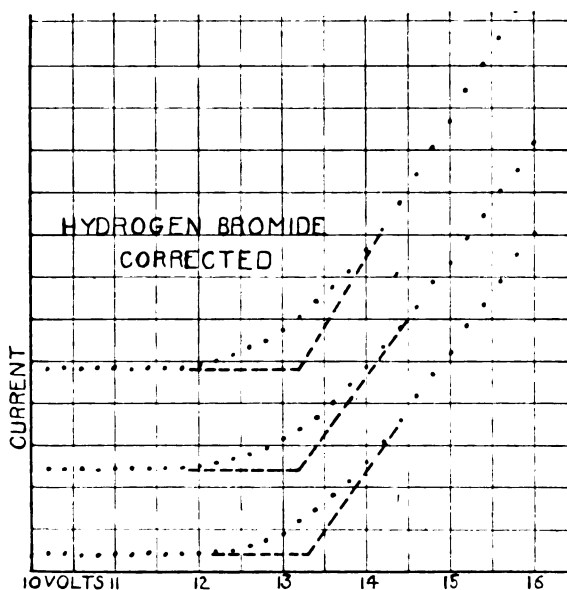
Fig. 3.



10 seconds for 20 cm. deflexion was necessary. The results were plotted, using the accelerating potentials as abscissæ, and the reciprocal of the rate of electrometer deflexion, which is proportional to the current reaching the negative electrode, as ordinates.

Typical curves are shown in figs. 2-4. They all had discontinuities, which meant that when the electrons acquired a certain kinetic energy, positive ions were produced and attracted to the negative electrode, which caused the rate of charging of the electrometer to increase suddenly. Since all the electrons did not have the same energy, the break in the curves was never sharp. The fastest electrons, which

Fig. 4.



produced the first ions, were relatively few in number, so that at first the change of slope increased slowly; but as more and more electrons became capable of producing ionization, the rate of change of slope greatly increased. This made it difficult to determine the exact point at which ionization began. If, however, tangents are drawn to the curve below and above a critical point, where the curve is practically a straight line, their intersection is quite definitely located by means of at least 6 or 8 points which determine the position of each tangent. From the method of correction adopted, any characteristic point, connected with the discontinuity in a curve which could be accurately fixed, was a satisfactory point. All that was needed was the difference between the breaks in the curve for helium and the gas in question.

*Phil. Mag.* Ser. 6. Vol. 46. No. 275. Nov. 1923. 3 H

Though the accelerating potential was increased up to 50 volts, in no case was more than one ionizing potential observed. If an electron produced ions by a second collision with a molecule, or if the molecule possessed two ionizing potentials, a second discontinuity might have been expected. Unless such an effect were very strong, it would not have produced a detectable bend in the curves, since the current due to the first ionization was already very large. All that can be stated from the present data is that any second ionization was too weak to be detected in the region up to 50 volts.

The results for the individual gases are as follows:—Mercury (chosen as a standard) 10·4 volts; helium 24·4, 24·4, 24·5, 24·5, 24·6, mean 24·5 volts; nitrogen 16·2, 16·3, 16·3, 16·3, mean 16·3 volts; hydrogen 15·6, 15·7, 15·9, 15·9, mean 15·8 volts; oxygen 12·4, 12·4, 12·5, 12·5, 12·6, 12·7, 12·7, mean 12·5 volts; hydrogen chloride 13·8, 13·8, 13·8, 13·9, mean 13·8 volts; hydrogen bromide 13·0, 13·2, 13·2, 13·2, 13·3, mean 13·2 volts; hydrogen iodide 12·6, 12·8, 12·8, 12·8, 12·9, mean 12·8 volts; ammonia 11·1, 11·1, 11·1, 11·2, mean 11·1 volts; water vapour 13·0, 13·2, 13·3, 13·4 volts, mean 13·2 volts.

In the Table (p. 835), these mean values are compared with the results of other measurements, together with calculated values of the ionizing potential when available.

The value for helium given by the present investigation agrees with the convergence limit of Lyman's spectroscopic series\*. It may be pointed out that with the present method it is unnecessary to assume Bohr's principle of selection, as has always been done heretofore, in order to correct the experimental results obtained for helium. The value for oxygen is considerably lower than that given by Foote and Möhler, but agrees with a value indicated on curves published by Hughes and Dixon but not reported by them†. There is good agreement between the calculated values for the halogen acids and the experimental results.

Throughout this investigation, Professor K. T. Compton has given many valuable suggestions and helpful criticisms, for which the writer wishes to express his appreciation.

\* Science, vol. lvi, p. 17 (1922).

† *Loc. cit.*





XVIII. *On the Theory of X-Ray Absorption and of the Continuous X-Ray Spectrum.* By H. A. KRAMERS, Copenhagen\*.

§ 1. *Definition of the problems and statement of the main results.*

THE origin of the absorption of homogeneous X-rays in matter may be traced to processes of two essentially different types. By the first of these the energy of the radiation is diminished as a consequence of processes of transference between two stationary states of the atoms, consisting in the removal of electrons from the interior of the atom (true absorption). By the second, the direction of propagation of the radiation is partly altered as a consequence of the reaction of the electrons in the atoms against the electrodynamic forces in the field of radiation (scattering). The mass-absorption coefficient may therefore be written in the well-known form

$$\frac{\mu}{\rho} = \frac{\tau}{\rho} + \frac{\sigma}{\rho}, \quad . . . . . (1)$$

where  $\mu$  is the coefficient of the observed absorption,  $\tau$  the coefficient of the true absorption, and  $\sigma$  the coefficient of absorption through scattering, while  $\rho$  is the density. Except for light elements and short wave-lengths,  $\tau$  is large compared with  $\sigma$ .

As well known, the observed absorption may with great approximation be considered as the sum of the absorbing actions of the individual atoms. The absorption due to a single atom may with great approximation be calculated from the observed value for  $\mu$  for an element by multiplying by the atomic weight  $A$  and dividing by Avogadro's number  $M$ . Writing  $\mu A/\rho M = \alpha_\mu$ ,  $\tau A/\rho M = \alpha_\tau$ , and  $\sigma A/\rho M = \alpha_\sigma$ , we have thus for the atomic absorption coefficient:

$$\alpha_\mu = \alpha_\tau + \alpha_\sigma, \quad . . . . . (2)$$

where  $\alpha_\tau$  corresponds to the true absorption and  $\alpha_\sigma$  to the scattering of the rays. The quantity  $\alpha$  has the dimensions of an area, and can be interpreted in the following way: Each atom acts as a small sphere of cross section  $\alpha$ , which absorbs completely all the rays which strike its surface. The quantity  $\alpha$  may therefore, with Lenard's terminology, be called the "effective cross section."

\* Communicated by Prof. N. Bohr.

The experimental results have shown\* that  $\alpha_\mu$  with considerable accuracy may be represented by

$$\alpha_\mu = CN^k\lambda^l + D(N), \quad \dots \quad (3)$$

where  $N$  is the atomic number and  $\lambda$  the wave-length.  $C$  is a constant independent of  $N$  and  $\lambda$ , which takes different values on the different sides of the characteristic absorption limits  $K, L, \dots$ ; while  $D$  depends on  $N$ . For the exponent  $k$ , the investigators give values between 3.5 and 4; while for  $l$  they give values between 2.5 and 3. In general, the second term on the right side of (3) is small compared with the first. For light elements and short wave-lengths, however, the second term may become much larger; and here the experimental value for  $D$  agrees† for light elements more or less closely with the theoretical value for the scattering from the electrons deduced by J. J. Thomson‡:

$$D(N) = \frac{8\pi}{3} \frac{e^4 N}{m^2 c^4} = 0.54 \cdot 10^{-24} \cdot N, \quad \dots \quad (4)$$

which has also been confirmed by Barkla's § direct experiments on the amount of scattering from light elements. Richtmeyer || represents for short wave-lengths the results of his absorption measurements with satisfactory accuracy by the formula

$$\alpha_\mu = CN^4\lambda^3 + D(N), \quad \dots \quad (5)$$

where  $C$  on the short wave-length side of the  $K$  limit has the value  $0.0229 \text{ cm.}^{-1}$  when  $\lambda$  is measured in  $\text{cm.}$ , while  $D$  for light elements does not differ much from the theoretical scattering coefficient (4). For heavier elements,  $D$  is several times larger. Also the scattering for these elements is several times larger than would correspond to (4), as was directly shown by Barkla and Miss Dunlop ¶, and as would be expected from the theory. It cannot be assumed, however, that Richtmeyer's  $D$  term just corresponds to the scattering coefficient  $\alpha_\sigma$ , because the theory as well as the experiment

\* W. H. Bragg and S. Peirce, *Phil. Mag.* xxvii. p. 626 (1914).  
A. Hull and M. Rice, *Phys. Rev.* viii. p. 326 (1916). R. Glocker, *Phys. Zeitschr.* xix. p. 71 (1918). E. A. Owen, *Proc. Roy. Soc.* xciv. pp. 339 and 510 (1918). Siegbahn and Wingårdh, *Phys. Zeitschr.* xxi. p. 83 (1920). F. K. Richtmeyer, *Phys. Rev.* xviii. p. 13 (1921). K. A. Wingårdh, *Zeitschr. f. Phys.* viii. p. 365 (1922), and Dissertation, Lund, 1923.

† Hull and Rice, *loc. cit.*

‡ J. J. Thomson, 'Conduction of Electricity through Gases,' p. 326 (Cambridge, 1907).

§ C. G. Barkla, *Phil. Mag.* vii. p. 543 (1904).

|| F. K. Richtmeyer, *loc. cit.*

¶ Barkla and Dunlop, *Phil. Mag.* xxxi. p. 222 (1916).

show that the scattering for the heavier elements increases with increasing wave-length. Wingårdh, in his dissertation\*, arrives at results which for short wave-lengths ( $\lambda < 0.35 \text{ \AA.}$ ) and elements with atomic number larger than 10 are represented by formula (5), where  $C$  on the short wave-length side of the K absorption limit has the value 0.0244 and on the long wave-length side a value about 5 to 7 times smaller, while  $D$  has the form  $3 \cdot 10^{-26} N^2$ .

The continuous X-ray spectrum has in the course of the last years been investigated by a number of physicists†. The problem is here to determine how, for a given tension on the tube and a given anticathode material, the energy in the continuous spectrum is distributed among different frequencies. As well known, this distribution varies with the angle which the direction in which the X-rays are observed makes with the direction of the cathode-rays‡. This distribution, especially for high tension, is not exactly symmetrical with regard to a plane perpendicular to the cathode-rays—a phenomenon which certainly may be ascribed to a kind of Doppler effect§. Kühlenkampff|| has recently made an extensive investigation of the continuous X-ray spectrum excited by rather low potentials (below 12,000 volts), and observed at an angle of about 90 degrees with the direction of the cathode rays. Calling the intensity of the part of the spectrum lying between  $\nu$  and  $\nu + d\nu$  by  $J_\nu d\nu$ , and denoting the quantum-theory limit of the continuous spectrum by  $\nu_0$ , which is related to the applied voltage  $V$  by the Einstein relation

$$h\nu_0 = Ve, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where  $e$  is the charge of the electron and  $h$  Planck's constant, Kühlenkampff represents his results rather closely by the formula

$$J_\nu = C\{N(\nu_0 - \nu) + N^2b\}, \quad . \quad . \quad . \quad (7)$$

holding for all values of  $\nu < \nu_0$ , while for  $\nu > \nu_0$  the intensity  $J_\nu$  is equal to zero.  $N$  represents the atomic number of the element of the anticathode. The constant  $b$  is about equal

\* *Loc. cit.*

† A most valuable survey of the experimental and theoretical work published until the fall of 1920 is given by D. L. Webster, "Problems of X-ray Emission," Bulletin of the National Research Council, vol. i. Part 7, Dec. 1920 (Washington), where also literature references are given. See also E. Wagner, *Jahrb. d. Rad. u. Elektr.* xvi. p. 190 (1919).

‡ C. E. Wagner, *Phys. Zeitschr.* xxi. p. 721 (1920).

§ Cf. A. Sommerfeld, *Phys. Zeitschr.* x. p. 969 (1909).

|| H. Kühlenkampff, *Ann. d. Phys.* lxi. p. 578 (1923).

to  $2.5 \cdot 10^{15}$  (if  $\nu$  is measured in  $\text{cm}^{-1}$ ). Kuhlenskampff emphasizes that the sharp bend in the intensity curve claimed by formula (7) is rather smooth in the experiment. The absolute value of  $C$  has not been determined by Kuhlenskampff, but can with some accuracy be found from experiments on the total X-ray emission under given conditions. The formulæ for the continuous X-ray spectrum proposed by Webster\* agree in the main with formula (7).

The object of the present paper is to show how it is possible to account theoretically for the main features of the phenomena of X-ray absorption and continuous X-ray emission discussed above. The explanation of these phenomena may be traced back to the determination of the radiation processes which may occur when a free electron of given velocity approaches a positive nucleus with given charge. The latter problem cannot at the present state of the quantum theory of radiation be solved in detail, but it will be shown how an application of the ideas underlying Bohr's correspondence principle enables us to obtain an approximative solution, which leads to very satisfactory results when applied to X-ray absorption and to the continuous X-ray spectrum. Thus the theory leads, in first approximation, to the following formula for the atomic true absorption coefficient:

$$\alpha_r = CN^4\lambda^3, \quad . . . . . (8)$$

where  $C$ , for wave-lengths shorter than the K limit, is given by

$$C = \frac{64\pi^4}{3} \frac{e^{10}m}{\sqrt{3} c^4 h^6} = g \cdot 0.0104 \quad . . . . (9)$$

( $e$  and  $m$  charge and mass of electron,  $c$  velocity of light,  $h$  Planck's constant). In this formula  $g$  is a numerical factor of the same order of magnitude as 1, whereas the experimental value, as mentioned, is equal to 0.023 to 0.025 †.

\* D. L. Webster, *Phys. Rev.* ix. p. 220 (1917).

† In the 11th chapter of 'Conduction of Electricity through Gases' J. J. Thomson has, by means of the classical theory of electrons, derived an expression for the absorption of X-rays on the basis of Stokes' ether pulse theory, by calculating the work which an electromagnetic pulse conveys to an electron which can perform harmonic oscillations round a position of equilibrium and which is originally at rest. The result depends essentially on the form of the pulse. If the pulse is assumed to be a "double" pulse—i. e., if its form is such that a short time-period  $\tau$  in which the electric force has one direction is followed by a period of the same length in which this force has the same magnitude but the opposite direction—the resultant absorption will be proportional

For the continuous X-ray spectrum, on the other hand, the following expression is obtained for the energy between  $\nu$  and  $\nu + d\nu$  radiated in all directions :

$$I_\nu = i \cdot \frac{8\pi}{3\sqrt{3}l} \frac{e^2 h}{c^3 m} \cdot N(\nu_0 - \nu) \sim i \cdot 5 \cdot 10^{-50} N(\nu_0 - \nu), \quad (10)$$

where  $i$  is the number of electrons striking the target in unit time, while  $l$  is a numerical factor of the order of magnitude 6. The formula (10) is very similar to the experimental formula (7) \*. Moreover, the numerical value of the coefficient is in satisfactory agreement with the experiments on the total efficiency of X-ray tubes.

§ 2. *The connexion between the probability of absorption of radiation and the probability of emission of radiation due to the capture of a free electron.*

On the quantum theory of radiation, the process of the absorption of X-rays must be considered as governed by the laws of probability in much the same way as absorption and emission of radiation are treated in Einstein's theory of temperature radiation †. Thus we must assume that when

to the cube of  $\tau$ . Identifying  $\tau$  with the period  $\lambda/c$  of a beam of homogeneous X-rays, and the natural frequency of the electron with the frequency of the K absorption limit, A. H. Compton (Phys. Rev. xiv. p. 249 (1919)) has shown that Thomson's formula can be written in the form.

$$\alpha = 32\pi^2 e^{10} m / c^4 h^6 \cdot N^4 \lambda^3,$$

which differs only from that given by (9) by the value of the numerical factor.

An attempt to account for the observed laws of absorption on the basis of our present views of the nature of X-rays and of the structure of the atom has recently been made by L. de Broglie (*Journ. de Phys.* iii. p. 33, 1922). Although this author arrives at a result which, just as Compton's formula, differs from (9) only by the value of the numerical factor, his treatment of the problem, which at all points differs essentially from that followed in this paper, seems not to be consistent with the way in which the quantum theory at present is applied to atomic problems. (Compare *Physikalische Berichte*, iv. p. 496, 1923.)

\* For earlier attempts to develop a theory of continuous X-ray emission, compare E. March, *Physik. Zeitschr.* xxii. pp. 209, 429 (1921); Bergen Davis, *Phys. Rev.* ix. p. 64 (1917); H. Brillouin, *Comptes Rendus*, clxx. p. 274 (1920); H. Behnken, *Zeitschr. f. Phys.* iv. p. 241 (1921).

† A. Einstein, *Phys. Zeitschr.* xviii. p. 127 (1917).

an atom is placed in a beam of homogeneous X-rays there exists a certain probability proportional to the intensity of the rays that within a given time-interval one of the electrons—for instance, a K electron—in the interior of the atom is expelled and leaves the atom with a velocity  $v$  determined by the Einstein relation :

$$h\nu = W + \frac{1}{2}mv^2, \quad . . . . . (11)$$

where  $\nu$  is the frequency of the incident rays and  $W$  the work necessary for the complete removal of the electron from the atom. The formula holds with neglect of terms of the order  $\left(\frac{v}{c}\right)^2$  and higher.

The quantum theory, in its present state, tells nothing about the mechanism of absorption and does not therefore permit the direct calculation of the probability that an absorption process may occur. By imagining, however, a thermodynamical equilibrium between atoms and free electrons on the one hand and temperature radiation in space on the other, it is possible to establish a relation between this probability of absorption and the probability of the inverse process, which consists in the binding of a free electron of velocity  $v$  by an atom in which a K electron is missing—a process which will be accompanied by the emission of radiation of frequency  $\nu$ . The relation thus obtained will be quite analogous to the relation between the probability of the occurrence of a spontaneous emission process and of an absorption process, obtained by Einstein in his above-mentioned theory of temperature radiation.

Let us for the sake of simplicity assume that there is a single neutral atom in a vessel of volume  $V$ , in which the temperature is equal to  $T$ . Then, according to Boltzmann's principle, the probability  $P_n$  that the atom is in its neutral normal state has a proportion to the probability  $P_v dv$  that a certain electron—for instance, a K electron—is missing and moves freely outside the ionized atom with a velocity lying between  $v$  and  $v + dv$  will be given by

$$P_n : P_v dv = ah^3 e^{\frac{h\nu}{kT}} : 4\pi V m^3 v^2 dv. \quad . . . . . (12)$$

$\nu$  has the same significance as in (11);  $ah^3$  represents the *a priori* probability for the electron under consideration

to be bound in the atom \*, so that  $a$  is a numerical factor ;  $k$  is Boltzmann's constant †.

We will now find a mathematical expression for the fact that the proportion given by (12) is not changed by the interaction with the field of radiation. For that purpose we will introduce—besides the effective cross-section  $\alpha_r$ , governing (in the way described, p. 836) the true absorption of rays by the normal atom leading to an expulsion of the electron—another effective cross-section  $\beta$  peculiar to the atom in the ionized state under consideration, which has the following significance:—The probability that, by a collision with the free electron, the ionized atom will bind this electron in its interior, accompanied by the spontaneous emission of a radiation quantum  $h\nu$ , is such that if the atom is imagined as a sphere of cross-section  $\beta$  the free electron will be bound by the atom if, and only if, it strikes the surface of this sphere.  $\beta$  is clearly seen to be a function of the velocity  $v$  and to depend on what kind of electron is missing in the ionized atom. The probability that the free electron moving with velocity  $v$  in a time-interval  $dt$  will be bound in the atom is obviously equal to

$$Q_{i \rightarrow n} dt = \frac{\beta r}{V} dt. \quad . \quad . \quad . \quad (13)$$

On the other hand, the probability that under the influence of the field of radiation the neutral atom in a time-interval  $dt$  will be ionized in such a way that the electron expelled has a velocity lying between  $v$  and  $v + dv$  is equal to

$$Q_{n \rightarrow i} dt dv = \alpha_r \frac{\rho(v, T) c dt}{h\nu} \frac{dv}{v}, \quad . \quad . \quad . \quad (14)$$

where  $\rho(v, T) dv$  represents the energy in the radiation field the frequency of which lies between  $\nu$  and  $\nu + d\nu$ . Assuming that the temperature is not so high that the temperature radiation will have a sensible influence on the processes

\* For instance, in an atom consisting of a nucleus and a single electron, where the stationary states are characterized in the well-known way by an integer  $n$ , the *a priori* probability of the  $n$ th state is equal to  $n(n+1)/k^2$ . (Compare Bohr, 'On the Quantum Theory of Line Spectra,' Copenhagen Academy (1918), Part ii, p. 76.)

† This method is seen to be essentially the same as that by means of which the chemical constant of gases and vapours may be theoretically derived, as well as the laws governing the emission of electrons from hot metals. In the treatment of these problems, however,  $a$  is often put equal to 1, an assumption for which in general no sufficient reason can be given. Cf. W. Schottky, *Phys. Zeitschr.* xxii. p. 1 (1921).

by which the free electron will be bound by the ionized atom (Einstein's "negative Einstrahlung"), and assuming for the function  $\rho(\nu, T)$  in the region of this temperature with sufficient approximation \*

$$\rho(\nu, T) = \frac{8\pi h\nu^3}{c^3} e^{-\frac{h\nu}{kT}}, \quad \dots \quad (15)$$

the thermodynamical claim that the probability proportion (12) is not changed by the interaction with the field of radiation assumes the form

$$P_n Q_{n \rightarrow i} = P_i Q_{i \rightarrow n}; \quad \dots \quad (16)$$

or, making use of (13), (14), and (15),

$$ah^3 e^{\frac{h\nu}{kT}} \cdot \alpha_r \frac{8\pi h\nu^3}{c^3} e^{-\frac{h\nu}{kT}} \frac{c}{h\nu} \frac{d\nu}{d\nu} = 4\pi V m^3 r^2 \cdot \frac{\beta_r}{V},$$

or, observing that by means of (11) we have  $\frac{d\nu}{d\nu} = \frac{mv}{h}$ ,

$$\alpha_r = \frac{m^2 v^2 c^2}{2ah^2 \nu^2} \beta_r, \quad \dots \quad (17)$$

in which formula  $r$  and  $\nu$  are connected by the relation (11).

### § 3. *The classical radiation from a free electron deflected by a positive nucleus.*

We shall now seek an expression for  $\beta$ , i. e. the efficient cross-section of the ionized atom with regard to free electrons which, by the emission of radiation, are bound by the atom in an orbit in its interior of the type considered. The quantum theory gives no information regarding the details of such an emission process: it claims only that the radiation is monochromatic and that the energy emitted amounts to a quantum  $h\nu$ . The only procedure which offers itself at present seems to consist in estimating the statistical result of a great number of such emission processes by investigating—in a way suggested by Bohr's correspondence principle—the radiation which on the classical electron theory would be emitted by the free electrons in consequence of the change in motion produced by the forces arising from the electric particles in the atom. In view of the approximative character of the results which may be obtained in this way, we are led in the treatment of

\* These assumptions do not, as will follow from a comparison with Einstein's cited paper, contain any restriction as regards the final result.



this problem to introduce a simplification which makes the electrodynamical problem much easier. Thus we shall confine ourselves to the consideration of the radiation which will be emitted by a free electron which "collides" with a single nucleus of charge  $Ne$ , *i.e.* which on its way approaches the nucleus so closely that its motion undergoes a considerable change.

Let the velocity of the electron before the collision be  $v$ , and let  $\rho$  designate the perpendicular distance of the nucleus from the original path of the electron. Disregarding the variation of the mass of the electron with its velocity, and assuming that the total loss of energy due to radiation is small compared with the kinetic energy  $\frac{1}{2}mv^2$ , the electron will describe a hyperbolic orbit with the nucleus at one of the foci. If the angle of deflexion of the electron is denoted by  $\pi - 2\phi_0$ , we have \*

$$\tan \phi_0 = \frac{m\rho v^2}{Ne^2}. \quad . \quad . \quad . \quad . \quad . \quad (18)$$

The amount of energy lost in unit time by the electron in the form of electromagnetic radiation is given by †

$$\frac{dR}{dt} = \frac{2e^2}{3c^3} j^2, \quad . \quad . \quad . \quad . \quad . \quad (19)$$

where  $j$  denotes the acceleration of the electron. The total loss of energy  $E$  due to radiation is found immediately by integrating the expression (19) over the time. If we call the eccentricity  $\epsilon$ , and if we describe the position of the electron in the plane of its orbit by means of polar coordinates  $r$  and  $\phi$ , where  $r$  is the distance from the nucleus and  $\phi$  the angular distance from the major axis, we have

$$\begin{aligned} \frac{1}{r} &= \frac{1 - \epsilon \cos \phi}{\rho \tan \phi_0}, \quad r^2 \dot{\phi} = \rho v, \quad \epsilon = \sec \phi_0, \quad j = \frac{N e^2}{m r^2}, \\ R &= \int_{-\infty}^{+\infty} \frac{2e^2}{3c^3} j^2 dt = \frac{2N^2 e^6}{3c^3 m^2} \int_{-\infty}^{+\infty} \frac{dt}{r^4} = \frac{2N^2 e^6}{3c^3 m^2 \rho v} \int_{\phi_0}^{2\pi - \phi_0} \frac{d\phi}{r^2} \\ &= \frac{2N^4 e^{10}}{3c^3 m^4 \rho^5 v^5} \int_{\phi_0}^{2\pi - \phi_0} \frac{d\phi}{(1 - \epsilon \cos \phi)^2}, \quad . \quad . \quad . \quad . \quad . \quad (20) \\ \int_{\phi_0}^{2\pi - \phi_0} (1 - \epsilon \cos \phi)^2 d\phi &= (2\pi - 2\phi_0)(1 + \sec^2 \phi_0/2) + 3 \tan \phi_0, \quad . \quad . \quad . \quad . \quad . \quad (21) \end{aligned}$$

\* Compare, for instance, E. Rutherford, *Phil. Mag.* xxi. p. 669 (1911).

† Compare, for instance, H. A. Lorentz, 'The Theory of Electrons,' p. 52 (2nd ed.).

Considering first the case where  $\phi$  is a small angle, i. e.,

$$\tan \phi_0 = \frac{mpv^2}{Ne^2} \ll 1, \quad . . . . . (22)$$

the integral (21) is in first approximation equal to  $3\pi$ , and with the same approximation the radiated energy becomes equal to

$$R = \frac{2\pi N^4 e^{10}}{c^3 m^4 p^5 v^5} . . . . . (23)$$

This energy is emitted as an electromagnetic aether pulse, the form of which can be found in the well-known way from the way in which the acceleration  $j$  changes with the time as regards direction and magnitude. In the case just considered, where the angle  $\phi_0$  is assumed to be small, the orbit of the electron will, especially in the neighbourhood of the nucleus, differ only little from a *parabolic Keplerian orbit*. On account of this, the investigation of the form of the pulse, and especially of the distribution of the energy emitted among different frequencies which will have special interest for us, can—for all values of  $N$ ,  $p$ , and  $r$  for which the derivation of formula (23) is justified—be reduced to the determination of the two functions which for one special parabolic orbit express the variation of the two components of the acceleration with the time.

Considering thus a parabolic Keplerian orbit for which the shortest distance between electron and nucleus is equal to  $\frac{1}{2}$ , and for which the angular momentum  $mpv$  of the electron with respect to the nucleus is equal to  $m$ , so that  $Ne^2/m=1$ , the polar coordinates  $r$  and  $\phi$  and the time  $t$  are simply expressed in terms of an auxiliary variable  $z$  by means of the formula :

$$t = \frac{1}{2} \left( \frac{z^3}{3} + z \right), \quad r = \frac{1+z^2}{2}, \quad \cos \phi = -\frac{1-z^2}{1+z^2}, \quad \sin \phi = \frac{2z}{1+z^2} . . . . . (24)$$

The components of the acceleration perpendicular to and parallel to the axis will be given by

$$j_{\text{perp.}} = -\frac{\sin \phi}{r^2} = \frac{8z}{(1+z^2)^3}, \quad j_{\text{par.}} = -\frac{\cos \phi}{r^2} = \frac{4(1-z^2)}{(1+z^2)^3} . . . . . (25)$$

In order to find how much of the energy radiated belongs to the different frequencies \*, the functions (25) must be

\* Cf. for instance J. H. Jeans, Phil. Mag. xx. p. 642 (1910).

developed in Fourier integrals:

$$j_{\text{perp.}}(t) = \int_0^\infty \phi(\gamma) \sin \gamma t d\gamma, \quad j_{\text{par.}}(t) = \int_0^\infty \psi(\gamma) \cos \gamma t d\gamma, \quad (26)$$

where

$$\phi(\gamma) = \frac{1}{\pi} \int_{-\infty}^{+\infty} j_{\text{perp.}}(\tau) \sin \gamma \tau d\tau, \quad \psi(\gamma) = \frac{1}{\pi} \int_{-\infty}^{+\infty} j_{\text{par.}}(\tau) \cos \gamma \tau d\tau, \quad (27)$$

and where in the two last integrals the time is denoted by  $\tau$ .

If in (27) we introduce  $z$  as integration variable by means of (24) and (25), we find, after some calculation,

$$\phi(\gamma) = \gamma i^{4/3} 3^{-1/2} H_{1,3}^{(1)}(i\gamma/3), \quad \psi(\gamma) = \gamma i^{5/3} 3^{-1/2} H_{2,3}^{(1)}(i\gamma/3). \quad (28)$$

In these formulæ  $H_p^{(1)}(x)$  denotes the Hankel function of the first kind and of the order  $p$ \*; from the properties of this function it will be seen that the given expressions are real for real values of  $\gamma$ . For small values of  $\gamma$  we have convergent expansions, the first two terms of which are given by

$$\begin{aligned} \phi(\gamma) &= 0.89\gamma^{2/3} - 0.41\gamma^{4/3} + \dots, \\ \psi(\gamma) &= 0.82\gamma^{1/3} - 0.22\gamma^{5/3} + \dots, \end{aligned}$$

while for big values of  $\gamma$  we have asymptotic expansions which begin as follows:

$$\begin{aligned} \phi(\gamma) &= \sqrt{\frac{2\gamma}{\pi}} e^{-\frac{\gamma}{3}} \left(1 - \frac{5}{24\gamma} + \dots\right), \\ \psi(\gamma) &= \sqrt{\frac{2\gamma}{\pi}} e^{-\frac{\gamma}{3}} \left(1 + \frac{7}{24\gamma} - \dots\right). \end{aligned}$$

Fig. 1 gives a graphical representation of the functions  $\phi$  and  $\psi$ .

For the total energy emitted we have

$$R = \frac{2e^2}{3c^3} \int_{-\infty}^{+\infty} (j_{\text{perp.}}^2 + j_{\text{par.}}^2) dt = \frac{2\pi e^2}{c^3} \quad (29)$$

On the other hand we have

$$\int_{-\infty}^{+\infty} (j_{\text{perp.}}^2 + j_{\text{par.}}^2) dt = \pi \int_0^\infty (\phi^2(\gamma) + \psi^2(\gamma)) d\gamma. \quad (30)$$

\*  $H_p^{(1)}(x) = \frac{i}{\sin p\pi} \{e^{-p\pi i} J_p(x) - J_{-p}(x)\}$  ( $p$  not integer), where  $J_p(x)$  is the ordinary Bessel function. This definition has been proposed by N. Nielsen, 'Handbuch der Zylinderfunktionen' (Leipzig, 1904). See further the very useful formulæ in Jahnke and Emde's *Funktionentafeln* (Leipzig, 1909).

We may therefore say that the relative amount of the radiated energy the frequency of which, multiplied by  $2\pi$ , lies between  $\gamma$  and  $\gamma + d\gamma$  is given by

$$P(\gamma)d\gamma = \frac{1}{3}(\phi^2(\gamma) + \psi^2(\gamma))d\gamma, \quad \int_0^\infty P(\gamma)d\gamma = 1. \quad (31)$$

Fig. 1.

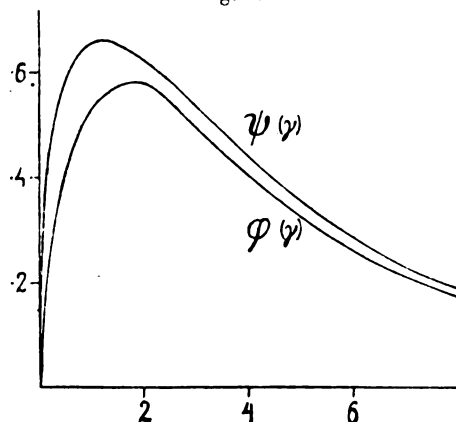


Fig. 2.

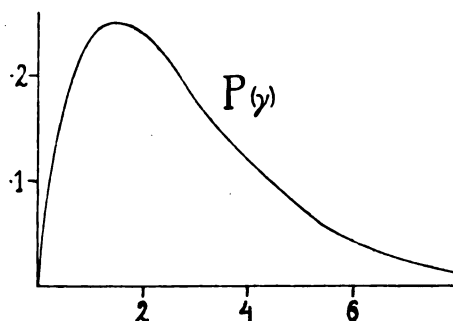


Fig. 2 gives a graphical representation of the function  $P(\gamma)$ , which has its maximum value in the neighbourhood of  $\gamma=1.5$ . In this connexion the value of the following integral may be noted, which follows directly from a general integration formula holding for all functions which, just as the Hankel functions, satisfy the Bessel differential equation\* :

$$\int_0^\infty \frac{P(\gamma)}{\gamma} d\gamma = \frac{4}{\pi\sqrt{3}}. \quad \dots \dots \dots (32)$$

\* Whittaker and Watson, 'Modern Analysis,' 3rd edition, p. 381, ex. 18; Jahnke and Emde, *loc. cit.* p. 166.

In the general case the shortest distance of the electron in its parabolic orbit from the nucleus is equal to  $\frac{mp^2v^2}{2Ne^2}$ , while the angular momentum of the electron round the nucleus is equal to  $mpv$ . Here it will obviously again be the function  $P(\gamma)$  which tells us how the energy is distributed on the different frequencies. We need only to calculate which value of the frequency  $\nu$  corresponds to a given value of  $\gamma$ . Now it is easily seen that the angular velocity in the pericentrum holding for the parabolic orbit defined by (24) is equal to 4, while for the general parabolic orbit it is equal to  $\frac{4N^2e^4}{m^2p^3r^3}$ . We may therefore directly put

$$\gamma = 2\pi\nu \frac{m^2p^3r^3}{N^2e^4} \quad \dots \quad (33)$$

It is of interest to remark that, for two parabolic orbits corresponding to the same angular momentum, *i. e.* to the same value of  $pr$ , the energy in the radiation lying between  $\nu$  and  $\nu + d\nu$  is the same. This follows directly from the circumstance that in (23) as well as in (33)  $p$  and  $r$  occur only in the combination  $pr$ .

In the foregoing we have established the formulæ by which is fixed the character of the energy-radiation which on the classical theory would take place from a parabolic orbit. In order that these formulæ hold, three conditions must be fulfilled:

- (a) In order that the orbit can be represented with sufficient accuracy as a parabola, the condition (22) must be fulfilled.
- (b) The total amount of energy radiated on the classical theory must be small compared with the kinetic energy of the electron:

$$\frac{2\pi N^4e^{10}}{c^3m^4p^5r^5} \ll \frac{1}{2}mv^2 \quad \dots \quad (34)$$

- (c) In order that the application of Newtonian mechanics may be justified, the velocity of the electron must, even in the point where it is largest, *i. e.* in the pericentrum, be small compared with the velocity of light:

$$\frac{2Ne^2}{mpr} \ll c \quad \dots \quad (35)$$

These conditions do not contradict each other. In fact, putting

$$\frac{mpv^2}{Ne^2} = A, \quad \frac{4\pi N^4 e^{10}}{c^3 m^5 p^5 v} = B, \quad \frac{2Ne^2}{cm pv} = C, \quad \dots \quad (36)$$

where A, B, and C are numerical quantities, we have

$$A^2 B = \frac{\pi}{2N} C^3, \quad \dots \quad (37)$$

showing that if conditions (a) and (b) are fulfilled ( $A \ll 1$ ,  $B \ll 1$ ), the condition (c) will in general also be satisfied.  
 P — We will now investigate the case where the angle  $\phi$  defined by (18) differs only little from  $\pi/2$ , i. e.

$$\tan \phi_0 = \frac{mpv^2}{Ne^2} \gg 1. \quad \dots \quad (38)$$

This corresponds to a hyperbolic orbit of the electron where the angle between the asymptotes is almost equal to  $180^\circ$ , i. e. where the electron describes an almost *rectilinear orbit*. The integral (21) reduces in this case in first approximation to  $\pi \sec^2 \phi_0/2$ , and the radiated energy (20) becomes equal to

$$R = \frac{\pi N^2 e^6}{3c^3 m^2 p^3 v}. \quad \dots \quad (39)$$

Just as in the case of a nearly parabolical orbit, the determination of the distribution of this energy for all values of N,  $p$ , and  $v$  satisfying (38) can be reduced to the determination of this energy distribution for one special rectilinear orbit. Considering thus an electron passing a positive nucleus at a distance  $p \gg 1$  and with a velocity numerically equal to  $p$ , the components of the acceleration of the electron perpendicular to and parallel to its path, considered as a function of the time, are respectively given by

$$j'_{\text{perp.}} = (1+t^2)^{-3/2}, \quad j'_{\text{par.}} = t(1+t^2)^{-3/2}, \quad \dots \quad (40)$$

if the nuclear charge is chosen such that  $Ne^2/m$  is numerically equal to  $p^2$ .

In analogy with our former procedure, the functions (40) must be developed in Fourier integrals:

$$j'_{\text{perp.}}(t) = \int_0^\infty \phi'(\gamma) \cos \gamma t \, d\gamma, \quad j'_{\text{par.}}(t) = \int_0^\infty \psi'(\gamma) \sin \gamma t \, d\gamma, \quad \dots \quad (41)$$

where

$$\phi'(\gamma) = \frac{1}{\pi} \int_{-\infty}^{+\infty} j'_{\text{perp.}}(\tau) \cos \gamma \tau \, d\tau, \quad \psi'(\gamma) = \frac{1}{\pi} \int_{-\infty}^{+\infty} j'_{\text{par.}}(\tau) \sin \gamma \tau \, d\tau, \quad \dots \quad (42)$$

where in the latter integrals the time is denoted by  $\tau$ . Introducing (40) we find the expressions :

$$\phi'(\gamma) = -\gamma H_1^{(1)}(i\gamma), \quad \psi'(\gamma) = i\gamma H_0^{(1)}(i\gamma), \quad (43)$$

involving the Hankel functions of the first kind of the order 1 and 0. For  $\gamma$  small we have the convergent expansions :

$$\begin{aligned} \phi' &= \frac{2}{\pi} + \frac{\gamma^2}{\pi} \left( \log \frac{\zeta\gamma}{2} - \frac{1}{2} \right) + \dots, \\ \psi' &= -\frac{2}{\pi} \gamma \log \frac{\zeta\gamma}{2} + \frac{\gamma^3}{2\pi} \left( 1 - \log \frac{\zeta\gamma}{2} \right) + \dots \\ &\quad (\log \zeta = 0.5772\dots). \end{aligned}$$

For large values of  $\gamma$  we have the asymptotic expansions :

$$\begin{aligned} \phi'(\gamma) &= \sqrt{\frac{2\gamma}{\pi}} e^{-\gamma} \left( 1 + \frac{3}{8}\gamma + \dots \right), \\ \psi'(\gamma) &= \sqrt{\frac{2\gamma}{\pi}} e^{-\gamma} \left( 1 - \frac{1}{8}\gamma + \dots \right). \end{aligned}$$

Fig. 3 gives a graphical representation of the functions  $\phi'$  and  $\psi'$ . For the total energy emitted we have :

$$R = \frac{2e^2}{3c^3} \int_{-\infty}^{+\infty} (j_{\text{perp}}'^2 + j_{\text{par}}'^2) dt = \frac{\pi e^2}{3c^3}.$$

With reference to (30) we may therefore say that the relative amount of the radiated energy the frequency of which, multiplied by  $2\pi$ , lies between  $\gamma$  and  $\gamma + d\gamma$  is given by

$$P'(\gamma) d\gamma = 2(\phi'^2 + \psi'^2) d\gamma, \quad \int_0^\infty P'(\gamma) d\gamma = 1. \quad (44)$$

Fig. 4 gives a graphical representation of  $P'(\gamma)$ .

In general, for an arbitrary set of values for  $N$ ,  $\rho$ , and  $\tau$  satisfying (38), the energy distribution is again given by (44), if  $\gamma$  is related to the frequency  $\nu$  by the relation

$$\gamma = 2\pi\nu \frac{p}{c}. \quad (45)$$

In order that these formulæ can be applied, three conditions must be fulfilled:

(a) The relation (38) must be fulfilled.

Fig. 3.

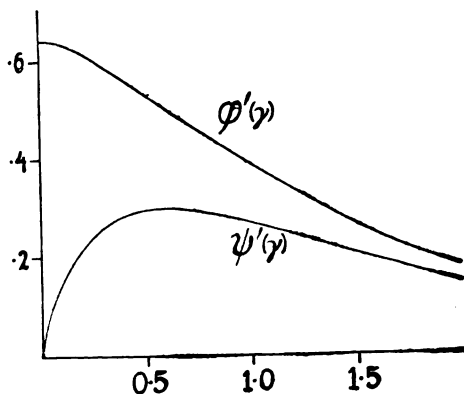
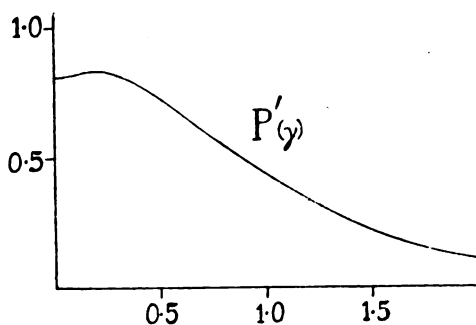


Fig. 4.



(b) The total amount of energy radiation must be small compared with the kinetic energy of the electron :

$$\frac{\pi N^2 e^6}{3c^3 m^2 \rho^3 v} \leq \frac{1}{2} m v^2. \quad . \quad . \quad . \quad (46)$$

(c) The velocity of the electron  $v$  must be small compared with the velocity of light.



Putting

$$\frac{N e^2}{m p v^2} = A', \quad \frac{2\pi N^2 e^6}{3 c^3 m^3 p^3 v^3} = B', \quad \frac{v}{c} = C', \quad \dots \quad (47)$$

where  $A'$ ,  $B'$ , and  $C'$  are numerical quantities, we see that

$$A'^3 C'^3 = \frac{3N}{2\pi} B', \quad \dots \quad (48)$$

showing that if the conditions (a) and (c) are fulfilled, the condition (b) will always be satisfied.

#### § 4. *The quantum theory radiation from a free electron colliding with a positive nucleus.*

With reference to the application of the quantum theory to radiation problems, we will assume that a free electron which collides with a positive nucleus may perform a transition to a stationary state of motion of less energy, accompanied by the emission of a quantum  $h\nu$  of monochromatic radiation. In the latter state the electron may either still be free—i.e. the electron may after the collision leave the nucleus with any velocity smaller than its original velocity—or the collision will result in the binding of the electron in one of the discrete series of elliptical or circular stationary states known from Bohr's theory of atomic structure. The statistical result of a large number of collisions with free electrons of the same velocity will therefore be the emission of a continuous spectrum, extending from very small frequencies to a limiting frequency  $\nu_0$  determined by  $h\nu_0 = \frac{1}{2}mv^2$ , and of a spectrum of discrete lines, extending from this limit towards larger frequencies\*. The line of highest frequency will correspond to a transition by which the electron is bound in a one-quantum orbit. In view of the correspondence principle, we are led to expect that the intensity distribution in this spectrum may be estimated from the intensity distribution in the radiation which the colliding electrons would emit on the classical theory. Thus with reference to the applications of the correspondence principle to series spectra, we should expect that every possible quantum transition corresponds to a certain frequency present in the motion of the electron, and that the probability for the occurrence of a transition process is closely connected with the amount of energy in the radiation which on the classical theory is correlated with the corresponding frequency.

\* Cf. N. Bohr, 'On the Quantum Theory of Line Spectra,' Copenhagen Academy, 1918, Part ii, p. 99.

Here we meet immediately the question, Which frequency in the motion corresponds to a given transition? In the present case the answer cannot be given in the same unambiguous way as was possible in the quantum theory of simple and multiple periodic systems, where the motion can be analysed in discrete harmonic components. If we confine ourselves, however, for the moment to those transitions where the electron is also free after the radiation process, the very simple assumption offers itself that the corresponding frequency is just equal to the frequency of the emitted radiation. As well known, such is not in general true for simple or multiple periodic systems where we have to do with discrete stationary states, but here there is at first sight nothing which prevents the introduction of such an assumption. It leads us immediately to the following way of estimating the probability for a transition by which the electron by performing a transition from one free state to another radiates a frequency  $\nu$ . Let again the nuclear charge be denoted by  $Ne$ , the velocity of the electron before the collision by  $v$ , and the distance from the nucleus to the original path of the electron by  $\rho$ , and let us suppose that the condition (22) is fulfilled. According to the formulæ (23), (31), and (33), the energy which on classical electrodynamics would be sent out in the form of radiation with frequencies lying between  $\nu$  and  $\nu + d\nu$  from a great number  $s$  of collisions of the same type will be equal to

$$s \cdot \frac{2\pi N^4 e^{10}}{c^3 m^4 \rho^3 v^3} P(\gamma) \frac{d\gamma}{d\nu} d\nu = s \cdot \frac{4\pi^2 N^2 e^6}{c^3 m^2 \rho^2 v^2} P\left(2\pi\nu \frac{\rho^3 v^3 m^2}{N^2 e^4}\right) d\nu. \quad (49)$$

Denoting, on the other hand, by  $q(\nu)d\nu$  the probability that a collision of the type considered gives rise to the emission of a radiation with frequency between  $\nu$  and  $\nu + d\nu$ , the correspondence principle leads us to the estimation that  $s \cdot q(\nu) h\nu d\nu$  is equal to the expression (49). We have of course not the least reason to expect that these two expressions will be exactly equal; thus we are, from the quantum theory of simple and multiple periodic systems, familiar with the idea that the initial state in a transition process is not sufficient in itself to determine the quantities which are characteristic of the process\*.

\* In this connexion it may be noted that a further support for the validity of our estimation may perhaps be derived in the case of transitions by which the angular momentum of the electron is not changed, since (as it has been remarked on p. 848) all nearly parabolic motions with the same angular momentum give rise to the same energy distribution in the classical radiation.

It seems difficult, however, at the present time to give a rational estimation of the quantity  $s.q(\nu)h\nu d\nu$  which may be regarded as more exact than that given above. We shall therefore write

$$q(\nu)h\nu d\nu \sim \frac{4\pi^2 N^2 e^6}{c^3 m^2 p^2 v^2} P \left( 2\pi\nu \frac{p^3 r^3 m^2}{N^2 e^4} \right) d\nu, \quad . \quad . \quad (50)$$

remembering that the  $\sim$  sign only means a first approximation.

Until now we have considered the case where  $mpr^2/Ne^2$  is small compared with unity (condition (22)). If, on the other hand, this quantity is large compared with unity (condition (38)) we have to apply the formulæ (39), (44), and (45) holding for the energy distribution in the radiation from a nearly rectilinear orbit, and an easy calculation shows that (50) must be replaced by

$$q(\nu)h\nu d\nu \sim \frac{2\pi^2 N^2 e^6}{3c^3 m^2 p^3 v^2} P' \left( 2\pi\nu \frac{p}{v} \right) d\nu. \quad . \quad . \quad (51)$$

See p. 6. The assumptions (50) and (51) lead to a definite theory for the continuous X-ray spectrum which will be considered in §6. Here we will proceed by putting the further question: How large will the probability be that the electron under consideration radiates so much energy that the collision results in its binding in one of the discrete stationary orbits round the nucleus? As mentioned above, the emission spectrum resulting from such collisions will consist of separate lines, and there can be no question of a simple correspondence with the frequencies occurring in the original motion of the electron. It is tempting, nevertheless, to extend here the considerations on which (50) and (51) were based, and to assume that a certain frequency interval in the radiation emitted on the classical theory corresponds with a process by which the electron is bound in a certain stationary state. The following way of estimating the magnitude of the corresponding interval immediately suggests itself. The energy with which the electron is bound by the nucleus in the  $n$ th stationary state is given by

$$W = \frac{2\pi^2 N^2 e^4 m}{n^2 h^2}, \quad . \quad . \quad . \quad (52)$$

which value has to be introduced in the expression (11) for the frequency emitted by the electron which is being bound. We will therefore assume that the corresponding

frequency interval can be approximately represented by

$$\Delta\nu \sim \frac{2\pi^2 N^2 e^4 m}{h^3} \left( \frac{1}{(n-\frac{1}{2})^2} - \frac{1}{(n+\frac{1}{2})^2} \right) \sim \frac{4\pi^2 N^2 e^4 m}{h^3 n^3}. \quad (53)$$

Denoting the probability for the occurrence of a process by which the originally free electron is bound in the  $n$ th quantum state by  $q_n$ , we can thus write approximately :

$$\begin{aligned} q_n h\nu &= \frac{4\pi^2 N^2 e^6}{c^3 m^2 p^2 v^2} P \left( 2\pi\nu \frac{p^3 v^3 m^2}{N^2 e^4} \right) \Delta\nu \\ &= \frac{16\pi^4 N^4 e^{10}}{c^3 m h^3 p^2 v^2 n^3} P \left( 2\pi\nu \frac{p^3 v^3 m^2}{N^2 e^4} \right), \quad \dots \quad (54) \end{aligned}$$

where we have assumed that  $P$  is sufficiently constant in the frequency interval  $\Delta\nu$ .

Assuming that, instead of (22), the condition (38) is fulfilled, (54) must be replaced by

$$q_n h\nu = \frac{8\pi^4 N^4 e^{10}}{3c^3 m h^3 p^2 v^2 n^3} P' \left( 2\pi\nu \frac{p}{v} \right). \quad \dots \quad (55)$$

Fig. 5.

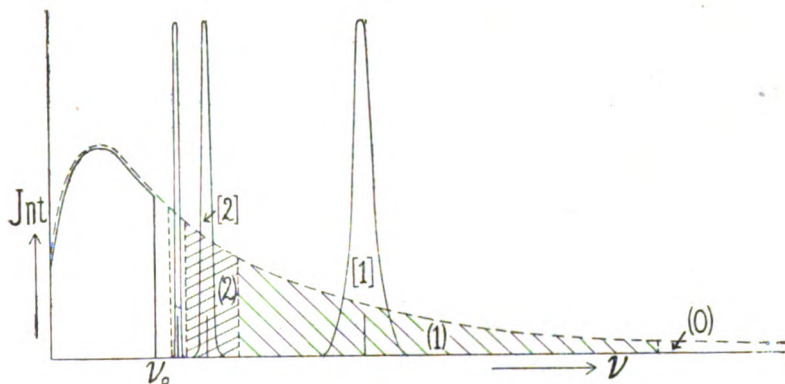


Fig. 5 illustrates the procedure followed. The dotted curve represents the energy distribution in the classical radiation; the full curves represent this distribution in the quantum problem. For frequencies smaller than the limit  $\nu_0$ , the two curves coincide. The frequency intervals which are assumed to correspond to the lines are separated by vertical dotted lines. According to our assumptions expressed in (54), the areas (1), (2), ... are equal to the areas [1], [2], .... That there will always be a large

frequency region extending to infinity in the classical energy distribution, which does not correspond to any transition, is a feature which has its analogy in the theory of simple and multiple periodic systems, where every possible radiation transition corresponds to an harmonic component in the motion, but not every harmonic component to a possible transition. Further, it needs hardly to be emphasized that there is a good deal of ambiguity in the choice for  $\Delta\nu$  expressed by (53), especially as regards the binding in the one-quantum state. This point will be of special interest in the discussion of the results. Another interesting point to which we should like to draw attention is the difference between the classical ideas and the quantum theory assumptions which comes to light in the problem treated here. In fact, while on the classical theory the result of the collision of an electron with a nucleus, which is characterized by given values of  $r$ ,  $p$ , and  $N$ , is uniquely determined, such a collision may on the quantum theory give rise to different results, the occurrence of which is governed by the laws of probability. Thus, after the collision the electron may either leave the nucleus with any velocity smaller than its original velocity or be bound by the nucleus in an  $n$ -quantum orbit. There will finally also be a finite probability for the electron not to radiate any energy at all. In our method of estimating the probabilities, this probability is clearly seen to be equal to the ratio of the part of the area of the dotted curve in fig. 5 designated by (0) to the total area of this curve. The probability that there occurs no radiation at all is therefore seen to become especially large for those values of the original angular momentum  $mpv$  of the electron for which the value of  $\gamma$  given by (33) becomes especially small\*.

#### § 5. *The atomic absorption coefficient for homogeneous X-rays.*

The formulæ of the former paragraph can be used for an approximate calculation of the efficient cross-section  $\beta$ , defined in § 2, which may be ascribed to a nucleus of charge  $Ne$  as regards its property of binding a free electron

\* In order to explain that in some cases moving electrons apparently may pass through an atom without being influenced by it at all, Franck has enunciated the hypothesis that electrons which at a collision do not radiate should not be deflected from their original path. The consequences of this hypothesis have been investigated by F. Hund, *Zeitschr. f. Phys.* xiii. p. 241 (1923).

in an  $n$ -quantum orbit. In fact, constructing a plane passing through the nucleus which is perpendicular to the direction of the free electron before the collision, every surface element  $d\sigma$  of this plane may be considered as contributing to the value of  $\beta$  with an amount equal to  $q_n d\sigma$ , where  $q_n$  is the quantity in formula (54) which depends on the distance  $p$  of the element  $d\sigma$  from the nucleus, and which determines the probability that a free electron the original path of which cuts  $d\sigma$  is captured in an  $n$ -quantum orbit. The total effective cross-section  $\beta$  may then be obtained by integrating  $q_n d\sigma$  over the whole plane. We thus obtain, making use of (54), (33), and (32),

$$\begin{aligned}\beta &= \int q_n d\sigma = 2\pi \int_0^\infty q_n p dp \\ &= \int_0^\infty \frac{32\pi^5 N^4 e^{10}}{c^3 m h^4 p v^2 n^3 \nu} P \left( \frac{2\pi \nu p^3 v^3 m^2}{N^2 e^4} \right) dp \\ &= \frac{32\pi^5 N^4 e^{10}}{3c^3 m h^4 v^2 n^3 \nu} \int_0^\infty \frac{P(\gamma)}{\gamma} d\gamma = \frac{128\pi^4 N^4 e^{10}}{3\sqrt{3} c^3 m h^4 v^2 n^3 \nu} \cdot \cdot \cdot \quad (56)\end{aligned}$$

It is of interest to mention that we obtain the same formula if we take into account the fact that the frequency interval (53) is finite, instead of assuming, as was done in (54), that it can be considered as very small.

In (56) we have integrated over all values of  $p$ , and of  $\gamma$ , from 0 to  $\infty$ , although formula (54) which has been used only holds in a certain limited region of  $p$  values. Thus (54) holds only as long as  $p$  is so small that  $m p v^2 / N e^2$  is small compared with unity, corresponding, on the classical theory, to a nearly parabolic orbit of the electron. On the other hand, for values of  $p$  for which this expression is large compared with 1, the classical orbit of the electron will be nearly rectilinear, and formula (55), instead of (54), could have been applied in the calculation of  $q_n p dp$ . As a sufficient approximation we will therefore use the following procedure. We shall consider a value  $p_0$  of  $p$  which makes  $m p v^2 / N e^2$  just equal to 1, and which is therefore given by

$$p_0 = \frac{N e^2}{m v^2} \cdot \cdot \cdot \cdot \cdot \cdot \quad (57)$$

For this value the classical orbit of the electron will be an equilateral hyperbola: for  $p_0 < 1$  the angle between the asymptotes is less than  $\pi/2$ , for  $p_0 > 1$  it will be larger

than  $\pi/2$ . Further, we will divide the integral  $\int_0^\infty q_n p dp$  in two parts,  $\int_0^{\gamma_0} q_n p dp$  and  $\int_{\gamma_0}^\infty q_n p dp$ , and apply (54) in the calculation of the former integral and (55) in the calculation of the latter. Introduced in (33), the expression (57) for  $\rho$  corresponds to a value of  $\gamma$  given by

$$\gamma_0 = \frac{2\pi\nu N e^2}{m v^3}, \quad . \quad . \quad . \quad . \quad . \quad (58)$$

while, introduced in (45), it corresponds to exactly the same value for  $\gamma$ . Proceeding in this way, and introducing (55) in the integral  $\int_{\gamma_0}^\infty q_n p dp$ , we see that (56) must be replaced by

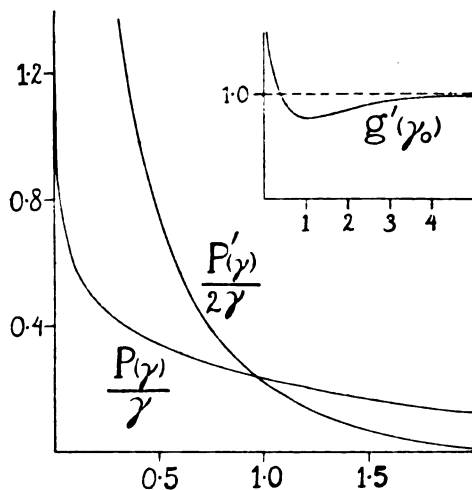
$$\beta = \frac{32\pi^5 N^4 e^{10}}{3c^3 m h^4 v^2 n^3 \nu} \left[ \int_0^{\gamma_0} \frac{P(\gamma)}{\gamma} d\gamma + \int_{\gamma_0}^\infty \frac{P'(\gamma)}{2\gamma} d\gamma \right]. \quad (59)$$

Comparing with (56), this formula may be written in the form

$$\beta = \frac{128\pi^4 N^4 e^{10}}{3\sqrt{3} c^3 m h^4 v^2 n^3 \nu} g'(\gamma_0), \quad . \quad . \quad . \quad (60)$$

where  $g'$  is a numerical factor, depending on  $\gamma_0$ , which is equal to the ratio of the sum of the two integrals appearing in (59) to the value which this sum assumes for  $\gamma_0 = \infty$ .

Fig. 6.



In order better to survey this result, we have in fig. 6 drawn curves representing  $P(\gamma)/\gamma$  as well as  $P'(\gamma)/2\gamma$  as

functions of  $\gamma$ . In the corner a graph of the function  $g'(\gamma_0)$  is represented, which can be expressed as a finite sum of squares and products of Hankel functions. For  $\gamma_0$  equal to zero,  $g'$  becomes infinitely large, due to the fact that the integral  $\int_{\gamma_0}^{\infty} P'(\gamma) d\gamma/2\gamma$  diverges when  $\gamma_0$  vanishes. In fact, for small  $\gamma_0$  this integral is equal to  $0.047 - 0.40 \log \gamma_0$ . We see that for  $\gamma_0 > 0.2$  the value of  $g'$  differs never more than 20 per cent. from unity, while for smaller values of  $\gamma_0$  it may become considerably larger.  $\gamma_0$  can also be written in the following form:

$$\gamma_0 = \frac{1}{2} \frac{\nu}{\nu_0} \sqrt{\frac{\nu_K}{\nu_0}}, \quad \dots \dots \dots (61)$$

where  $\nu_0$  is the frequency "corresponding" to an energy quantum  $\frac{1}{2}mv^2$ , according to the formula

$$h\nu_0 = \frac{1}{2}mv^2, \quad \dots \dots \dots (62)$$

while  $\nu_K$  is the frequency corresponding to the energy with which the electron is bound in a 1-quantum orbit,

$$\nu_K = \frac{2\pi^2 N^2 e^4 m}{h^3}. \quad \dots \dots \dots (63)$$

This frequency coincides closely with the frequency of the K-absorption limit. The frequency  $\nu$  entering in the expression for  $\beta$  is (cf. (11)) obviously connected with  $\nu_0$  and  $\nu_K$  by the relation

$$\nu = \nu_0 + \frac{\nu_K}{n^3}. \quad \dots \dots \dots (64)$$

Before proceeding, we must still consider two errors involved in the deduction of (60), referring to the conditions (b) and (c) on p. 848 and p. 851. In fact, for given  $N$  and  $v$  our formula (54) for  $q_n$  obtained from the consideration of a parabolic orbit loses its validity for small values of  $p$ , since the radiation in the classical orbit will no longer be small (condition (34)), and since the velocity of the electron no longer remains small compared with the velocity of light (condition (35)). In consequence of this there will be a region of  $p$  values, extending from zero, for which the value of the integrand in (59) may involve a considerable error. Elimination of  $p$  between (33) and the second of the formulæ (36) shows, however, that in the region of  $\nu$  and  $N$  values covered by the experiment ( $\lambda > 0.1 \text{ \AA}$ ,  $N < 93$ ) the error due to the first of the causes mentioned above may be neglected except for small values of  $v$ , i. e. for small values of the ratio  $\nu_0/\nu$ . On the



other hand, the influence of the second cause (large velocity of the electron) may for large  $N$  and especially for large  $v$  and  $\nu$  have some effect on the final result.

Attention must further be drawn to a possible source of error of another kind. We must expect that, by the emission of radiation, the angular momentum of the electron round the nucleus cannot change by more than  $h/2\pi$  \*. Now the possible values of the angular momentum of an electron bound in an  $n$ -quantum orbit are equal to  $1, 2, 3, \dots, n$ . It would therefore seem reasonable to extend the integral (56) in (59) not to  $\infty$  but to an upper limit  $p_1$  corresponding to an angular momentum  $mpr$  equal to  $(n+1)h/2\pi$ . It can, however, readily be shown that this would influence the final result very little. In fact the upper limit  $p_1$  for  $p$ , to be introduced in the integration (59), is found by introducing  $p_1 = (n+1)h/2\pi mr$  in (33) or in (45) according as  $p_1 < p_0$  or  $p_1 > p_0$  (cf. p. 857), or, what is the same, according as  $\nu_0/\nu_k < 1/(n+1)^2$  or  $\nu_0/\nu_k > 1/(n+1)^2$ . Restricting ourselves here to the latter case, the upper limit  $\gamma_1$  in the integral  $\int_{\gamma_0}^{\gamma_1} P'(\gamma) d\gamma/2\gamma$  is easily seen to be equal to  $\frac{\nu}{\nu_0} \frac{n+1}{2}$ , and therefore always larger than  $(n+1)/2$ . From the curve for  $P'(\gamma)/2\gamma$  it is seen that the introduction of this upper limit instead of  $\infty$  will never influence the value of  $\beta$  materially.

It is seen that the errors which are introduced on account of the conditions (22) or (38) and (35) not being fulfilled are only due to the introduction of purely mathematical simplifications, and therefore might be discarded by a more elaborate analytical treatment in which the orbits are no longer considered as either parabolic or rectilinear, and in which relativity dynamics are used throughout †. On

\* N. Bohr, 'On the Quantum Theory of Line Spectra,' Copenhagen Academy, 1918, Part I. p. 34; A. Rubinowicz, *Physikal. Zeitschr.* xix. pp. 441, 465 (1918).

† Note added during the proof.—If the calculations are carried through, without the introduction of any restrictions regarding the value of the  $\phi_0$  in (18), we meet with Hankel functions the order of which is expressed by a complex number. The final result for the value of  $\beta$  is found to be of the form (60), where

$$g'(\gamma_0) = \frac{\pi}{4} \sqrt[3]{\gamma_0} H_{i\gamma_0}^{(1)}(i\gamma_0) H_{i\gamma_0}^{(1)}(i\gamma_0). \quad \left( H_p^{(1)}(r) = \frac{dH_p^{(1)}(r)}{dr} \right).$$

The graph of  $g'(\gamma_0)$  given in figure 6 agrees rather closely with this expression. For large values of  $\gamma_0$  it can asymptotically be represented by  $1 - 0.218\gamma_0^{-2/3}$ , while for small values of  $\gamma_0$  it becomes equal to  $-\frac{\sqrt[3]{3}}{\pi} (1 + \pi\gamma_0) \log \frac{\gamma_0}{2}$  if terms containing second and higher powers of  $\gamma_0$  are omitted.

the other hand the errors in the region of small values of  $\nu_0/\nu$ , which will be due to the conditions (34) or (46) not being fulfilled, are inherent in the method.

After these digressions referring to the limits of the validity of our formulæ, we will now proceed to determine the atomic absorption coefficient  $\alpha_r$  for X-rays referring to an atom consisting of a nucleus which has bound one electron in an  $n$ -quantum orbit. This coefficient, according to our considerations in § 2, will be closely connected with the probability that a nucleus captures a free electron and binds it in such an orbit. From (17) and (60) we have thus :

$$\alpha_r = \frac{m^2 r^2 c^2}{2 a h^2 \nu^2} \beta = \frac{64 \pi^4 N^4 e^{10} m}{3 \sqrt{3} \cdot a_n c h^6 n^3 \nu^3} g' = \frac{64 \pi^4 e^{10} m}{3 \sqrt{3} c^4 h^6} g' \frac{N^4 \lambda^3}{a_n n^3} \\ = 0.0104 \cdot g' \frac{N^4 \lambda^3}{a_n n^3}, \quad (65)$$

where we have introduced the wave-length  $\lambda$  (measured in cm.), and where  $a_n$ , the statistical weight of the atom in its  $n$ -quantum state, is equal to  $n(n+1)$ .

Formula (65) may be used to find an expression for the effective absorbing cross-section of *neutral atoms* for homogeneous X-rays. In fact, we may assume that the probability for the expulsion of a K, L, or M electron from the interior of a neutral atom by means of X-rays in first approximation will be the same as the probability of expelling from an atom containing only one electron an electron from a 1-, 2-, or 3-quantum orbit. Denoting by  $b_n$  the number of electrons present in  $n$ -quantum orbits, we get thus the following expression for the atomic (true) absorption coefficient for an element of atomic number  $N$  :

$$\alpha_r = g \cdot 0.0104 N^4 \lambda^3, \quad (66)$$

$$g = g' \left( \frac{b_1}{a_1} + \frac{b_2}{8a_2} + \frac{b_3}{27a_3} + \dots \right), \quad (67)$$

where the first term in the brackets corresponds to the K-group, the second to the L-group, etc. This formula should of course hold only for wave-lengths shorter than the K-limit  $L_K$ ; for wave-lengths longer than  $L_K$  but shorter than  $L_L$ , the first term in the expression for  $g$  should be omitted; for wave-lengths longer than  $L_L$  but shorter than  $L_M$ , the two first terms should be omitted; etc.

As regards the application of formula (67), several points are to be observed. First of all we meet the question

whether it is justifiable to consider the different electrons in the same group as independent of each other, and to ascribe a statistical weight  $n(n+1)h^3$  to each of them, disregarding the division of the groups into sub-groups. In order to investigate this problem, let us consider the case of an atom containing one electron which is exposed to an external field of force, *e.g.* a homogeneous magnetic field. Taking, moreover, the relativity modifications in the laws of mechanics into account, the orbit of the electron in the stationary state will be described, besides by the principal quantum number  $n$ , by two auxiliary quantum numbers, in such a way that each stationary state corresponding to a given value of  $n$  appears split up into  $n(n+1)$  states corresponding to slightly different values of the energy, and each possessing a statistical weight  $h^3$ . Considering one of these states, we may again define an efficient cross-section  $\beta$  governing the probability that a free electron colliding with the nucleus is bound in this state with the emission of radiation, and an efficient cross-section  $\alpha$  governing the probability that the electron in this state is expelled from the atom due to incident monochromatic radiation. The relation between  $\alpha$  and  $\beta$  will be given by (17) if  $a$  in this formula is put equal to 1 instead of  $n(n+1)$ . On the other hand, if we apply our method of estimating the value of  $\beta$  we are led to an expression for this quantity which is  $n(n+1)$  times smaller than that given by (60). In fact, the frequency-interval which was defined by (53) corresponds to a binding of the electron in *any*  $n$ -quantum orbit, and must therefore in the present case be divided by the number indicating in how many states of equal weight the  $n$ -quantum state is split up. This may be illustrated by observing that when the  $n$ -quantum state is split up in different sub-states under the influence of the external field, the tendency for the colliding electron to be bound in this or in that sub-state will depend on the orientation of its original path with respect to the nucleus and the direction of the field. From these considerations it is seen that the value of  $\alpha$  will always be the same as that given by (65), whether regard is taken of the sub-states or not.

The assumption that in the problem of the removal of an electron from a completed group in the *neutral* atom the same formula (65) may still be applied to each electron in the group, and with the same value of  $a_n$ , is made highly probable by arguments of similar nature. Thus, considering for instance the K-group, the ratio between the statical

weight of the atom in its neutral state and in an ionized state in which one electron is removed is no longer  $2/h^3$ , but less than that (probably  $\frac{1}{2}h^3$ \*). On the other hand, a free electron colliding with the ionized atom will by no means have the same chance of being captured in a 1-quantum orbit as in the case of a collision with a free nucleus. In fact, such a capturing process can only take place for especially favourable orientations of the original path of the colliding electron with respect to the orbit of the K-electron already present in the atom, and it is reasonable to expect that this effect will just cancel out the other effect which was due to the statistical weight.

As well known, the L, M, ... absorption limits consist actually each of several limits lying close to each other; this fine-structure is intimately connected with the division of the electron groups in the atom into sub-groups; but certain difficulties are still involved in its detailed interpretation†. The determination of the contributions of the different L-limits, M-limits, etc. to the total L-absorption, M-absorption, etc. lies outside the scope of our present considerations.

Another point which needs consideration when formula (67) is applied, is that the different terms on the right side of (67) can only be expected to hold if the corresponding group of electrons is well in the interior of the atom, so that the energy with which these electrons are bound differs only little from the binding of an electron in an orbit of the same quantum number by a free nucleus. If the sum in (67) is also extended to the outer groups of the atom, the terms corresponding to these groups will be very inaccurate and probably too large. We may expect that here also errors in our expressions for  $\beta$  will come in, which are due to the fact that in § 3, instead of considering the binding of an electron by an atom which has lost one electron, we considered the binding by an atom which has lost all its electrons. On the total amount of absorption these errors have, however, little influence, at any rate for small wave-lengths, since the absorption due to the inner groups is much larger than that due to the outer groups.

Introducing in (67) the values  $b_1=2$ ,  $b_2=8$ ,  $b_3=18$ , which according to Bohr's theory are the number of electrons present in the K, L, and M groups, for all elements for which  $N \gg 29$ , we get

$$g = g'(1 + \frac{1}{6} + \frac{1}{18} + \dots). \quad (68)$$

\* Cf. N. Bohr, *Ann. der Physik*, lxxi. p. 271 (1923).

† Cf. N. Bohr and D. Coster, *Zeitschr. für Physik*, xii. p. 342 (1923).

The first term, which is due to the absorption of the K electrons, is seen to be preponderant over the following terms. This is in agreement with the experiments, which have shown that there is a very great difference in the absorption coefficient on both sides of the K-limit. While for the elements from molybdenum (42) to tin (50) the ratio between the  $\alpha$ -values on the short and long wave-length side of this limit amounts to about 6:1\*, there are also values in the literature for such a heavy element as lead ( $N=82$ ) (3.5:1)†, and such a light element as aluminium ( $N=13$ ) (11:1)‡; but the two latter ratios, which are each only based on a single observation, are extremely uncertain. On our formula we should expect a ratio of about 5.5:1 for heavy elements, while for light elements, due to the errors just mentioned, this ratio might be expected to be somewhat larger. The agreement must be considered satisfactory, especially if we remember how large an ambiguity there is involved in our fixation of the  $\Delta\nu$ -value for a one-quantum orbit in (53), as a consequence of which there is a rather big uncertainty in the ratio between the first two terms in (68).

If we bear in mind the approximative character of the whole method of estimating probabilities, and remember that the factor  $g'$  in general does not differ much from unity (cf. p. 859), we arrive at the conclusion that for wave-lengths shorter than the K-limit the expression (66) may be expected to hold with a value for  $g$  which has the same order of magnitude as unity. The agreement with the empirical formula (5) is very satisfactory, especially if we remember that the measured absorption coefficients cover a region in which the lowest values are several hundred times smaller than the biggest values. The observed value for C (0.0229 [Richtmeyer] or 0.0244 [Wingårdh]) corresponds to a value for  $g$  equal to 2.2 or 2.4.

Many authors have found that for a given element or for a given wave-length the observations are better described by an exponent of  $\lambda$  somewhat less than 3, or an exponent of  $N$  somewhat less than 4§, proving that

\* Glocker, *Physikal. Zeitschr.* xix. p. 71 (1918); F. K. Richtmeyer, *Phys. Rev.* xviii. p. 13 (1921); K. A. Wingårdh, Dissertation, Lund, 1923. The values given in literature vary between 5.5 and 7: compare Williams and Worsnop, *Nature*, cviii. p. 306 (1921).

† Hull and Rice, *Phys. Rev.* viii. p. 326 (1916); comp. also Williams and Worsnop, *loc. cit.*

‡ C. D. Miller, *Phys. Rev.* viii. p. 329 (1916).

§ Compare the papers cited on p. 837.

formula (5) only can be considered as a first approximation. Richtmeyer remarks especially that for wavelengths not much shorter than the K-limit, his formula gives values which are too high. This may be due to the mathematical simplifications introduced in our calculations, and may also be connected with the circumstance that just in this region the theory on which our formulæ are based may be expected to fail in principle (compare p. 860).

### § 6. *The Energy Distribution in the continuous X-ray Spectrum.*

Formulæ (50) and (51) in § 4 give expressions for the energy distribution in the radiation which will ensue from the collision of a great number of electrons possessing the velocity  $v$  with nuclei of charge  $Ne$ , if the distance from the nucleus to the original path of the colliding electron is equal to  $p$ . As explained on p. 852, these formulæ may be expected to hold approximately for frequencies smaller than the limit  $\nu_0$  given by (62); for larger frequencies the spectrum will consist of a series of discrete lines. To a first approximation we may assume that also the spectrum excited by swift electrons colliding with *neutral* atoms may be calculated in the same way, with the difference of course that no frequencies will be emitted larger than the limit  $\nu_0$ . This assumption finds a justification, discussed below in more detail, that, as a consequence of it, most of the radiation is contributed by electrons penetrating right into the interior of the atom, where the influence of the other electrons compared with that of the nucleus is very small.

We shall first consider the radiation which would be emitted in one second from a surface element  $d\sigma$  of an infinitely thin target containing  $A$  atoms of atomic number  $N$  per  $\text{cm}^2$ , which is bombarded by a beam of cathode rays of velocity  $v$  in which  $s$  electrons in one second pass across a cross-section of  $1 \text{ cm}^2$ . The energy  $i_\nu d\sigma d\nu$  in this radiation which lies between frequencies  $\nu$  and  $\nu + d\nu$  will obviously be given by an integral:

$$i_\nu d\sigma d\nu = s \cdot A d\sigma d\nu \int_0^\infty 2\pi p q(\nu) h\nu dp, \quad \dots \quad (69)$$

where  $q(\nu)h\nu$  is given by the expressions (50) or (51). Introducing the expression (50), *i.e.* assuming that the

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condition (22) is fulfilled with sufficient approximation, we get

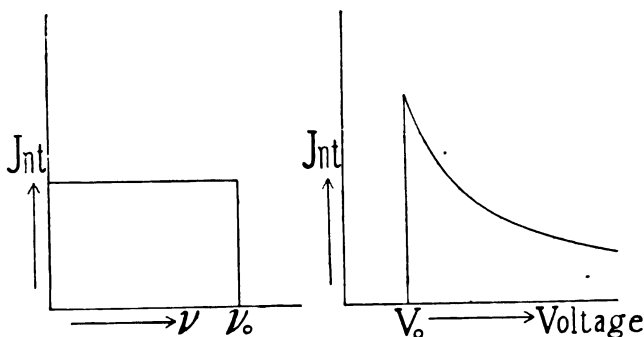
$$i_\nu d\sigma d\nu = sA d\sigma d\nu \int_0^\infty \frac{8\pi^3 N^2 e^6}{c^3 m^2 \nu^2} P\left(2\pi\nu \frac{\rho^3 r^3 m^2}{2N^2 e^4}\right) d\rho. \quad (70)$$

Introducing the quantity  $\gamma$ , given by (33), as integration variable, we get

$$\begin{aligned} i_\nu d\sigma d\nu &= sA d\sigma d\nu \frac{8\pi^3 N^2 e^6}{3c^3 m^2 \nu^2} \int_0^\infty \frac{P(\gamma)}{\gamma} d\gamma \\ &= \frac{32\pi^2}{3\sqrt{3}} \frac{N^2 e^6}{c^3 m^2 \nu^2} s \cdot A d\sigma d\nu. \quad \dots \quad (71) \end{aligned}$$

This expression does not contain  $\nu$ , so that  $i_\nu$  has a constant value for frequencies between zero and the Duane-Hunt limit  $\nu_0$ , while it is zero for  $\nu > \nu_0$ . A graphical representation is given on the left side of fig. 7. On the right

Fig. 7.



side the form of the theoretical "isochromate" in the spectrum of the infinitely thin target is given, which gives the dependency of the energy of a given small frequency interval on the voltage applied. Since the voltage is proportional to the square of the velocity, the isochromate will have the form of a piece of an hyperbola which starts from the minimum voltage  $V_0$  at which the radiation of the frequency considered can be excited\*.

In the deduction of (71) it was assumed that in the integral (69) the classical orbit of the electron could, with

\* Compare D. L. Webster and A. E. Hennings, *Phys. Rev.* **xxi**, p. 312 (1923), where the corresponding curves for an infinitely thin target are drawn, derived by means of the Thomson-Whiddington law from the experiments.

sufficient approximation, be considered as parabolic (condition (22)). For increasing values of  $p$ , however, the orbit will become hyperbolic and finally become nearly rectilinear. We shall apply the same procedure as that applied in the former paragraph, *i. e.*, we shall divide the integral (69) in two parts—one extended over  $p$  values for which the angle between the asymptotes is less than  $90^\circ$ , using the expression (50) for  $q(\nu)$ , and one extended over  $p$  values for which this angle is larger than  $90^\circ$  and in which the expression (51) for  $q(\nu)$  is used. This means that the integral in (71) must be replaced by the sum of the two integrals appearing in (59), where  $\gamma_0$  is again defined by (58) or (61). Introducing, just as on p. 858, the quantity  $g'$ , the only change which must be made in formula (71) consists in the addition of the factor  $g'$ . Since the latter quantity varies only slightly with varying  $\gamma_0$ , *i. e.* with varying  $\nu$ ,  $\nu_0$ , and  $N$ , this addition does not affect the results materially, and in the following formulæ the factor  $g'$  will be omitted.

An easy calculation shows that the integrand in (69) takes its maximum value for  $p$  equal to about  $p_K \sqrt{\frac{\nu_K}{\nu_0}} \sqrt[3]{\frac{2\nu_K}{\nu}}$ , where  $p_K$  denotes the radius of the orbit of a K electron, while for  $p$  twice as large the relative magnitude of the integrand has become very small. This shows that the observed radiation is mainly due to electrons which penetrate right into the interior of the atom. In fact, choosing a very unfavourable case—*i. e.* a heavy element (Pt) and a low voltage (7000 volt,  $\lambda_0 = c/\nu_0 = 1.18 \text{ \AA.}$ ), and a rather long wavelength ( $\lambda = c/\nu = 1.7 \text{ \AA.}$ ),—we find that the maximum in question lies at about  $p = 11 p_K$ . This distance corresponds to the region of the M electrons where the screening action of the inner electrons on the colliding electron is still small.

In the experiments on the continuous X-ray spectrum we have to do with a target of finite thickness in which the cathode rays penetrate, losing kinetic energy on their way through the atoms. The loss of energy will be due to the emission of X-rays only to a very small extent; its main cause is the expulsion of electrons from the interior of the atom, which will give rise to the emission of characteristic X-ray radiation. The latter problem has recently been theoretically investigated in detail by Rosseland\*, who was able to account for the laws holding for the dependency of

\* S. Rosseland, Phil. Mag. xlv. p. 65 (1923).



the intensity of the characteristic X-rays on the voltage applied. Rosseland's considerations are based on Bohr's theory for the stopping of swiftly-moving electrified particles through matter\*, which gives a rational theoretical explanation of the well-known Thomson-Whiddington law. This law states that the decrease of the velocity of an electrical particle in matter is governed by the formula

$$\frac{dv}{dx} = -a, \quad . \quad . \quad . \quad . \quad . \quad . \quad (72)$$

where  $dx$  is an element of the path of the particle, while  $a$  is a constant characteristic for the substance. Bohr gives a theoretical formula for  $a$  which in the case of  $\beta$  rays and cathode rays assumes the form :

$$a = \frac{16\pi e^4 A}{m^2} \sum_i \log \left( \frac{kr^3 m}{4\pi v_i e^2} \right). \quad . \quad . \quad . \quad . \quad (73)$$

Here  $A$  denotes the number of atoms in unit volume, while  $k$  is a numerical constant equal to 1.1. The summation has to be extended over all electrons in the atom;  $v_i$  is a quantity of the same order of magnitude as the frequency of revolution of the electron round the nucleus. Assuming a kind of mean value  $\bar{v}_i$  of the  $v_i$ -values of the different electrons, (73) may be written :

$$a = \frac{16\pi e^4 ANl}{m^2} = 1.957 \cdot 10^{42} \frac{A}{M} Nl, \quad . \quad . \quad . \quad (74)$$

where  $N$  is the atomic number and  $M$  Avogadro's number, while  $l$  has the dimensions of a number and is equal to  $\log(kr^3 m/4\pi v_i e^2)$ . Due to the logarithm,  $l$  depends only slightly on  $v$ , nor is it very sensitive to our assumptions on the value of  $v_i$ . Thus for a value of  $v$  corresponding to 10,000 volts, and taking  $\bar{v}_i = 10^{17}$ , we get  $l = 6.6$ . When the velocity has decreased to 5000 volts,  $l$  decreases by about 1, while the assumption that  $\bar{v}_i$  is 2.72 times larger causes also a decrease of  $l$  by 1. Thomson-Whiddington's law agrees very well with the experiments†. As regards the value of  $a$ , the recent experiments by Terrill‡ on Be, Al, Ca, Ag, and Au are in very good agreement with Bohr's theory. Thus the empirical values of  $l$  for these elements are equal to 5.9, 5.5, 5.5, 5.8, and 7.3.

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\* N. Bohr, Phil. Mag. xxv, p. 10 (1913) and xxx, p. 281 (1915).

† R. Whiddington, Proc. Roy. Soc. lxxxvi, p. 360 (1912).

‡ H. M. Terrill, Phys. Rev. xxi, p. 476 (1923). The recent experiments of B. F. J. Schonland (Proc. Roy. Soc. civ. p. 235 (1923)) on the range of cathode rays in Al, Cu, Ag, and Au foils give also a very close confirmation of Bohr's theory.

Returning now to the continuous X-ray spectrum, the spectrum emitted from a finite target will be obtained by summing the radiations which will be emitted by the electrons at the various stages of their velocity in the target. Denoting the energy between  $\nu$  and  $\nu + d\nu$  in the total radiation per second by  $I_\nu d\sigma d\nu$ , the quantity  $I_\nu$  can obviously be derived from the intensity function (71) for an infinitely thin target by means of the integral

$$I_\nu = \int_{r_0}^{r_\nu} i_\nu \frac{dx}{dr} dv = - \int_{r_0}^{r_\nu} i_\nu \frac{4c^3}{a} dv, \quad . \quad . \quad (75)$$

where  $r_0$  is the original velocity of the electrons, while  $r_\nu$  means the velocity for which  $h\nu = \frac{1}{2}mv_\nu^2$ . Introducing the expression (71) for  $i_\nu$ , and the expression (74) for  $a$ , we have

$$\begin{aligned} I_\nu &= - \int_{r_0}^{r_\nu} \frac{32\pi^2 N^2 e^6}{3\sqrt{3} c^3 m^2 r^2} \cdot s \cdot A \cdot \frac{4c^3 m^2}{16\pi e^4 A N l} dv \\ &= -s \int_{r_0}^{r_\nu} \frac{8\pi}{3\sqrt{3} l} \frac{e^2}{c^3} N r dv = s \cdot \frac{4\pi}{3\sqrt{3} l} \frac{e^2}{c^3} N (v_0^2 - r_\nu^2). \end{aligned}$$

Introducing instead of  $r_0$  and  $r_\nu$  the frequency  $\nu_0$  of the Duane-Hunt limit ( $\frac{1}{2}mv_0^2 = h\nu_0$ ) and the frequency  $\nu$  we get, putting  $l=6$ ,

$$I_\nu = s \cdot \frac{8\pi}{3\sqrt{3} l} \frac{e^2 h}{c^3 m} N (\nu_0 - \nu) = s \cdot 4.95 \cdot 10^{-50} N (\nu_0 - \nu), \quad . \quad . \quad (76)$$

which is identical with formula (1C), given in the first paragraph, and is in general agreement with the experiments.

In the foregoing calculation two factors have been neglected. Firstly the absorption of rays in the target, which originate from atoms in the interior of the target. Kühlenkampff as well as Webster have, however, made corrections for this absorption\*. Secondly, the electrons will not only lose kinetic energy at their collisions with the atoms but they will also be deflected through large angles, so that in general they will penetrate much less deeply into the target than when their path was straight†. Due to these deflexions, a fraction of the electrons will be able to leave the target ("reflexion" of cathode rays‡), some of them with very small velocities, but many of them

\* D. L. Webster and A. E. Hennings, *Phys. Rev.* xxi. p. 301 (1923).

† Compare D. L. Webster and A. E. Hennings, *loc. cit.*

‡ Cf. A. Becker, *Ann. d. Phys.* xvii. pp. 387, 447 (1905); A. Kovarik, *Phil. Mag.* xx. pp. 849, 866 (1910); B. F. J. Schonland, *loc. cit.* p. 240.

also with velocities about equal to the initial velocity  $v_0$ . The latter effect increases considerably with the atomic number, and will materially contribute to the appearance of the "bend" in Kuhlenskampff's curves, for which the second term on the right hand of (7) gives an approximate expression.

The problem of the differences in the intensity distributions in the radiations which are observed at different angles with the direction of the cathode rays\*, claims obviously a closer examination of these deflexions in the target. In fact, the spectrum due to an infinitely thin target will, as seen from the difference in the curves  $\phi(\gamma)$  and  $\psi(\gamma)$ , or  $\phi'(\gamma)$  and  $\psi'(\gamma)$ , (compare figs. 1 and 3), in general be different when observed in different directions. For targets of finite thickness this effect will no longer appear in the radiation due to electrons which have lost a part of their original velocity, since, due to the deflexions, the directions of the motions of these will be distributed almost at random.

We will not enter here on this problem, nor will we discuss the difficult question (mentioned on p. 838) of the asymmetry of the radiation with respect to a plane perpendicular to the cathode rays†. We shall here only draw attention to an important question which we meet with when considering more closely the assumptions underlying our calculations. Thus we have, as stated in the beginning of § 4, assumed that any radiation takes place by the emission of monochromatic quanta  $h\nu$ . This assumption, which is so essential in the applications of the quantum theory to line spectra, can no doubt also be applied to a process where a free electron is bound by an atom with emission of radiation. This seems to follow directly from photoelectric phenomena, especially from M. de Broglie's beautiful experiments‡. In the case of a free electron which loses so little energy by a collision that it leaves the atom again with a finite velocity, the assumption in question cannot be tested directly however, and the time which the collision takes is so short—presumably much shorter than the time which the emission of a monochromatic quantum  $h\nu$  necessarily must take—that it at first sight would seem uncertain whether Bohr's frequency relation can be applied also here. Notwithstanding these difficulties there seems on the other hand to be no reason

\* Compare Wagner, *Phys. Zeitschr.* xxi. p. 621 (1920).

† See N. Bohr, *Zeitschr. f. Phys.* xiii. p. 154 (1923).

‡ See, for instance, the Report of the Solvay Conference held at Brussels in 1921.

to be afraid that the estimation in § 4 of the intensity distribution in the continuous spectrum, which forms the basis of the calculations in this paragraph, should be less valid. In fact, the success of the applications of the correspondence principle makes it extremely probable that a comparison with the radiation which would be emitted on the classical theory will always afford a method of determining approximately the energy distribution in the actual radiation.

Finally we will apply the formulæ of this paragraph to the calculation of the total amount of radiation. From (76) we find that the radiation energy which in the mean will be due to the impact of a single electron on the target, is equal to

$$I = \frac{8\pi}{3\sqrt{3}l} \frac{e^2 h}{c^3 m} \int_0^{v_0} N(v_0 - v) dv = \frac{4\pi}{3\sqrt{3}l} \frac{e^2 h}{c^3 m} N v_0^2 \\ = \frac{\pi}{3\sqrt{3}l} \cdot \frac{e^2 m}{c^3 h} N v^4. \quad (77)$$

The ratio to the kinetic energy  $\frac{1}{2}mv^2$  of the electron will give the efficiency coefficient of the X-ray tube:

$$\text{Eff.} = \frac{2\pi}{3\sqrt{3}l} \frac{e^2}{ch} N \left(\frac{v}{c}\right)^2 = 2.34 \cdot 10^{-4} N \left(\frac{v}{c}\right)^2. \quad (78)$$

The efficiency of X-ray production has been investigated by many physicists\*. Beatty† has deduced from his experiments the following approximate formula for the efficiency:

$$\text{Eff.} = 2.54 \cdot 10^{-4} B \left(\frac{v}{c}\right)^2, \quad . . . . (79)$$

where B is the atomic weight, which is about equal to 2N. The agreement must be considered satisfactory, if we remember that in the deduction of (78) a large number of factors are neglected. For the first, we have disregarded the absorption in the target itself and in the walls of the tube, by which a good deal of energy is lost, especially in the region corresponding to small frequencies. Secondly, we have disregarded the characteristic radiation, which is quite of the same order of magnitude as the continuous radiation, and the intensity of which is also roughly proportional to the fourth power of the velocity of the cathode rays‡.

\* Compare the survey given by Bergen Davis, Bulletin of the National Research Council, vol. i. Part 7 (Dec. 1920).

† R. T. Beatty, Proc. Roy. Soc. lxxxix. p. 314 (1913).

‡ Compare S. Rosseland, Phil. Mag. xlv. p. 65 (1923).

XCIV. *Critical Electron Energies in Hydrogen.* By FRANK HORTON, *Sc.D., F.R.S.*, and ANN CATHERINE DAVIES, *D.Sc.\**

IN the Proceedings of the Royal Society, A, vol. xvii. p. 1 (1920) the authors have given an account of an investigation of critical electron energy values in hydrogen. The experiments described in this paper were carried out in order to ascertain whether the positive ions which could be detected leaving a positively charged platinum surface under electronic bombardment could be attributed to hydrogen occluded in the metal, but the results obtained afforded no support for such a view. From the experiments in hydrogen it was concluded that there are two critical electron energies at which radiation is produced, and two at which ionization occurs, and from the approximate agreement between the values obtained and the values predicted from Bohr's theory, the first radiation voltage and the first ionization voltage were attributed to the hydrogen atom, and the other two critical values to the hydrogen molecule. It was assumed that at the higher ionization voltage the molecules are dissociated into pairs of atoms and that one atom of each pair is ionized. As the experiments in hydrogen were performed mainly with a view to comparing the critical points obtained in the gas with the point at which a positive ion current commenced under the electronic bombardment of the platinum gauze in a high vacuum, the investigation was not extended to applied accelerating voltages greater than 20, and the determination of the absolute values of critical points was only approximate.

During the past year the authors have carried out a much fuller investigation of the effects of electron collisions with hydrogen, partly with a view to ascertaining the critical electron energy values more accurately than was possible with the apparatus used in the earlier research, but mainly in the hope of determining experimentally whether the radiation or ionization occurring at a critical stage is of atomic or of molecular origin. The method used for testing the origin of a radiation was to ascertain whether it could be absorbed and re-emitted by the gas in its normal state. This test was made by investigating whether the radiation in question would travel through the gas and produce a photo-electric effect on an electrode so placed that it could not be illuminated either directly, or by reflexion, from the position

\* Communicated by the Authors.

at which the exciting electron collisions occurred. As hydrogen in the normal state is in the molecular condition, such a "handing-on" of radiation cannot occur if the radiation is produced by dissociation of the molecule into atoms and the excitation of one of these atoms, but only if the radiation is of true molecular origin. The test of the nature of the positive ions produced at a critical ionization stage was a spectroscopic examination of the radiation produced when recombination occurs, the assumption being made that the Balmer lines are due to the recombination of electrons and positive hydrogen atoms and that they therefore only appear if atoms are present.

Since the completion of our earlier research several investigations of the effects of electron bombardment of hydrogen have appeared\*. Of these, the investigations by Duffendack and by Olmstead, which have been published while the present investigation was in progress, are particularly interesting in that they are attempts to distinguish the critical energy stages which are due to the molecule from those which are due to the atom. Olmstead's experiments enabled him to attribute certain energy stages definitely to collisions of electrons with molecules, but they did not provide any experimental basis for distinguishing between the molecular energy stages at which dissociation occurs and those at which no dissociation takes place. Duffendack's experiments, which were of a spectroscopic nature, led him to conclude that the ionization which is produced at 16 volts results from collisions of electrons and hydrogen molecules, at which dissociation of the molecule into atoms and the ionization of one of these atoms occurs. The reason for this conclusion was that when the arc is in hydrogen was obtained at 16 volts, not only the secondary spectrum lines but also the Balmer series lines were present, indicating the presence of hydrogen atoms.

The present experiments have indicated that the following voltages correspond to critical electron energy values in hydrogen:—10.2 volts, 11.9 volts, 12.6 volts, 13.5 volts, 15.9 volts, 22.8 volts, 26.1 volts, and 29.4 volts. At the

\* J. Franck, P. Knipping, and Thén Kruger, *Deutsch. Phys. Ges. Verh.* xxi. p. 728 (1919); C. Found, *Phys. Rev.* xvi. p. 41 (1920); F. L. Mohler and P. D. Foote, *Sci. Papers, Bur. of Stan.* 400, p. 669 (1920); F. L. Mohler, P. D. Foote, and E. H. Kurth, *Phys. Rev.* xix. p. 414 (1922); K. T. Compton and P. S. Olmstead, *Phys. Rev.* xvii. p. 45 (1921); P. E. Boucher, *Phys. Rev.* xix. p. 189 (1922); P. S. Olmstead, *Phys. Rev.* xx. p. 613 (1922); O. S. Duffendack, *Phys. Rev.* xx. p. 665 (1922).

critical values 10.2 volts, 11.9 volts, 12.6 volts, and 26.1 volts an increased rate of production of radiation commences, while at the values 13.5 volts, 15.9 volts, and 29.4 volts an increased rate of production of ionization commences. At 22.8 volts the bombarding electrons suffer inelastic collisions, but these are not accompanied by the production of more radiation or more ionization. The experiments indicate that 10.2 volts and 13.5 volts are atomic critical points, and that 11.9 volts, 12.6 volts, 15.9 volts, and 22.8 volts are molecular critical points. They show that the radiation produced at 11.9 volts can be "handed on" throughout a volume of the gas, and that it is therefore due to an excitation of a molecule without dissociation. They confirm Duffendack's observation that the Balmer series lines appear at the 16-volts ionization stage and show, therefore, that at this stage the dissociation of the molecule into atoms and the ionization of one of these atoms occurs.

A blue glow, whose spectrum was continuous and extended from the yellow to the limit of the visible spectrum in the violet, was obtained at lower voltages than either the Balmer lines or the lines of the hydrogen secondary spectrum, and without any ionization occurring. The experimental evidence suggests that this continuous spectrum is to be attributed to the formation of molecules ( $H_2$  or possibly  $H_3$ ) by the combination of neutral atoms produced by electronic-molecular encounters which result in dissociation and atomic excitation.

The results obtained are consistent with the view suggested by Pauli\* from theoretical considerations, that the ionization of the hydrogen molecule by the process  $H_2 \rightarrow H_2^+ + \text{electron}$  requires about 23 volts energy, whereas by the process  $H_2 \rightarrow H + H^+ + \text{electron}$  it requires considerably less energy.

#### *Description of Apparatus.*

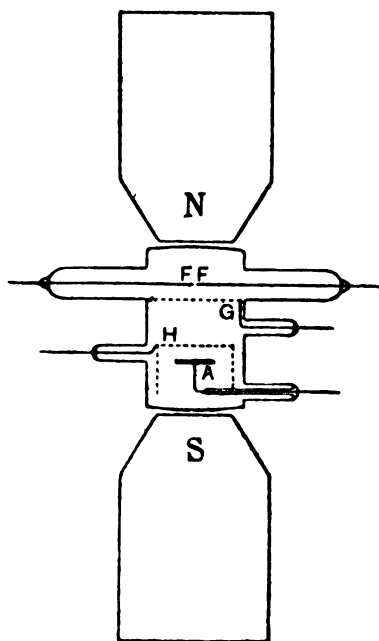
Three forms of apparatus were employed in the present series of experiments, two for the spectroscopic investigation, and one for the accurate location of the critical electron energy values and the investigation of the origin of the various radiations. The latter form of apparatus is identical with that employed by the authors in their experiments on the "handing-on" of radiation in helium, and is described in detail in a former paper†. Those employed

\* W. Pauli, Jr., *Ann. der Phys.* lxxiii. p. 177 (1922).

† Phil. Mag. xlii. p. 746 (1921).

for the spectroscopic investigation have also been used by the authors in previous researches\* and will therefore be only briefly referred to here. Fig. 1, which is reproduced from the Proceedings of the Royal Society, A, vol. cii. (1922), indicates the arrangement of electrodes used in one of these forms. This apparatus was so constructed that it could be placed between the poles of a strong electromagnet whereby a concentration of the luminosity into a bright column parallel to the slit of the spectroscope could be effected.

Fig. 1.



The filaments F, F, only one of which was used at a time, were platinum strips coated with a mixture of lime and baryta, and the other electrodes were of platinum. The spectroscope was placed so as to view the part of the tube between G and H in the direction of the lengths of the filaments, the maximum intensity of luminosity being thus in line with a vertical plane through the axis of the collimator.

The other form of apparatus used for the spectroscopic

\* Proc. Roy. Soc. A, c. p. 599 (1922), and cii. p. 131 (1922).



investigation was designed for the production of arcs at low voltages, and was a two-electrode tube with a filament of tungsten and a spherical platinum anode whose distance from the filament could be varied from 1 mm. to 20 mm.

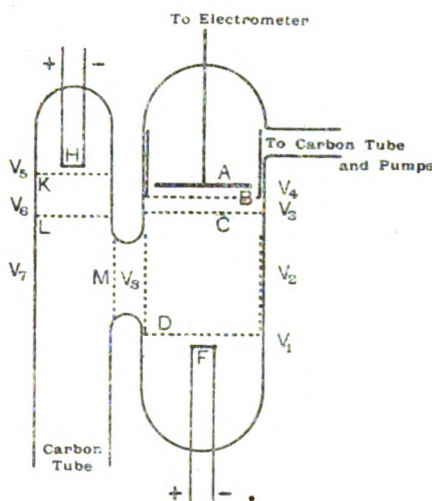
Experiments with the form of apparatus represented in fig. 1 were carried out with two different arrangements of electric fields. In both cases the electrons from the hot filament were accelerated towards the gauze G by means of a difference of potential which could be altered in steps of one-tenth of a volt. A milliammeter (or a galvanometer) included in this circuit measured the total current emitted by the filament. In one case the remaining electrodes H and A were maintained at the same potential as G, so as to cause electronic-molecular encounters to occur in a region where the bombarding electrons suffer no change of velocity except that due to their collisions with the gas. In the other case a difference of potential was applied between G and H in such a direction as to oppose the progress of electrons from the filament to the gauze H. By making this difference of potential larger than that applied between F and G, and including a sensitive galvanometer in the circuit between G and H, a measure of the ionization current corresponding to any value of the electron energy could be obtained. The former arrangement is preferable when it is desired to determine what are the minimum electron energies required for the production of particular spectrum lines, but the latter arrangement is a ready means of determining, in a qualitative manner, whether different parts of a spectrum require different amounts of energy for their excitation; for where such differences occur, the column of glow extending for part of the distance between G and H can be made to show different colours at different distances below G.

The value of the electron energy for any given value of the applied potential difference accelerating the electrons from the filament was obtained by adding to the applied potential difference a correction which was determined in each case by the methods which we have indicated in the former papers already referred to.

The two forms of apparatus used in the spectroscopic investigation were connected together and were supplied with hydrogen from the same storage bulb. The arrangements for circulating the pure gas through the apparatus were the same as those employed in our earlier investigations. The hydrogen entered the discharge tubes through a U-tube containing coconut charcoal and immersed in liquid air.

Fig. 2 is a diagrammatic representation of the apparatus used for the investigation of the origin of the radiations produced at the various critical voltages. It consists of two vertical discharge-tubes connected by a short horizontal tube. The two tungsten filaments, which are the sources of the bombarding electrons, are at F and H, the former, F, being situated at the bottom of the main tube (on the right-hand side of the figure), and the latter, H, at the top of the side tube. All the other electrodes are of platinum and are arranged as shown in the diagram. For convenience of reference, the electric fields between adjacent electrodes will

Fig. 2.



be referred to as  $V_1$ ,  $V_2$ , etc., as indicated in the figure. The design of the apparatus makes it impossible for any radiation produced in the space between the gauzes K and L to illuminate the collecting electrode A or the electrode B directly, and it reduces to a minimum the possibility of radiation which originates between K and L being reflected by the glass walls and metal parts of the apparatus so as to illuminate A or B. The extent to which such radiation was reflected round so as to illuminate A or B was investigated by special experiments. These were carried out by using the general X-radiation produced by electronic bombardment of the gauze K in the highest obtainable vacuum, and by investigating the effect produced by this radiation

on the electrodes A and B when the electric fields were so arranged that no electrons or positive ions, which might possibly be knocked out of the various gauzes by bombardment, could reach the collecting electrode A. It was found that, even when the filament H was heated to the limit of safety and a very considerable amount of radiation was being produced in the side tube, no photo-electric effect of this radiation on either A or B could ever be detected. On the assumption that a given electron emission from the side filament H, with a given energy of bombardment, produces the same amount of radiation as an equal emission from the lower filament F does under the same applied potential difference, it was possible to estimate what fraction of the amount of radiation produced would have to be reflected round in order to give a detectable effect. By using an electron current from the lower filament equal to the maximum electron current ever used from the side filament, it was found in this way that if any radiation were reflected round so as to illuminate A, such reflected radiation was less than 1 part in 100,000 of that produced.

The hydrogen used in the experiments was prepared by the electrolysis of a solution of barium hydrate in water, and was dried before it entered the storage bulbs by passing it through a little coconut charcoal in a U-tube immersed in liquid air. The gas was admitted to the apparatus of fig. 2 through a coconut charcoal tube, cooled in liquid air, attached to the discharge tube shown on the left-hand side of the figure, and it could be pumped out through a similar U-tube connected to the main tube of the apparatus. In some of the experiments the gas was slowly streaming through the apparatus during the observations.

Before admitting hydrogen to any of the discharge tubes the residual gas was removed as completely as possible from the electrodes and glass walls by prolonged heating and pumping with a mercury vapour pump, the filaments being maintained glowing during the process.

#### *Location of Critical Electron Energy Values.*

The values of the critical electron energies for the production of radiation and of ionization in hydrogen were first carefully investigated by means of the apparatus indicated in fig. 2, using electrons from the lower filament F, and varying the energy of these by gradually increasing the field  $V_1$ . Series of observations of the currents to various electrodes were taken for different values of  $V_1$  with three

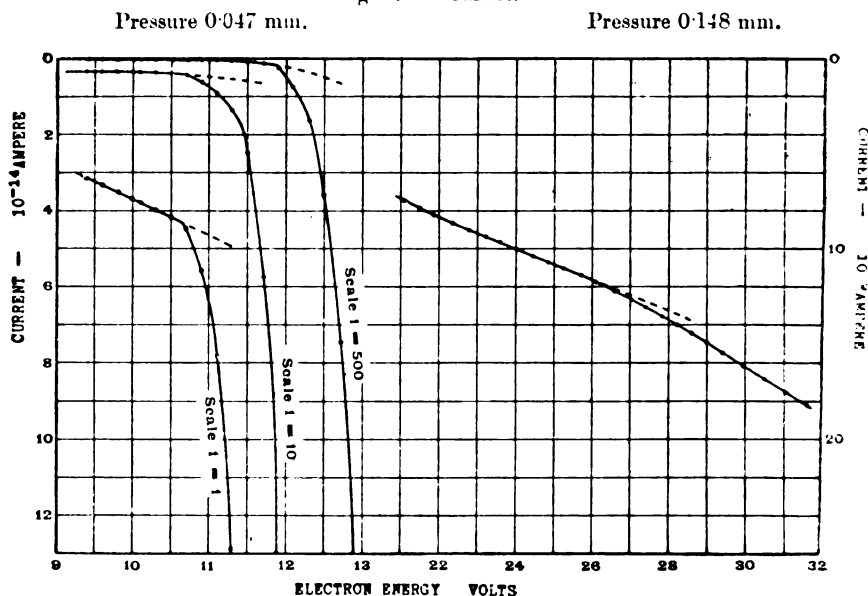
different arrangements of electric fields, which may be designated as arrangements for obtaining (a) Radiation, or R, curves, (b) Curves distinguishing between ionization and radiation, or (I-R) curves, (c) Inelastic collision curves. In taking observations of the type (a) or (b), the potential difference  $V_2$  was arranged so as to oppose electrons from the filament, its value remaining constant during any one set of observations, but varying in different experiments from zero to 20 volts. The electrons from the filament encountered a larger constant retarding difference of potential in the space between the gauzes C and B, and were prevented from reaching the level of B. This difference of potential,  $V_3$ , tends, of course, to drive any positive ions produced between B and C, or any which diffuse into this space from below, towards the gauze B. In arrangements for obtaining R curves, the field  $V_4$  was made larger than  $(V_2 + V_3)$  and was in the reverse direction to these fields, so as to prevent any positive ions from reaching the collecting electrode A. Any photo-electrically active radiation produced by the collisions of electrons with gas molecules would cause electrons to leave the upper surface of the gauze B and the attached cylinder, which are negatively charged with respect to A. Hence the only current reaching the collecting electrode in such circumstances is that carried by these photo-electrons from B. Discontinuities in the current-potential difference curves obtained with this arrangement of fields therefore indicate the critical values of the electron energy at which different types of collision resulting in the emission of radiation occur.

For obtaining (I-R) curves the only respect in which the arrangement of fields differed from that already described was that the difference of potential  $V_4$  was very much smaller (about 2 volts or less). Such a small difference of potential would not prevent the positive ions which passed through the gauze B from reaching A and charging the electrometer positively, but it would still cause the photo-electric effect of the radiation to result in a charging of the electrometer negatively. Curves taken with such an arrangement of fields therefore indicate critical electron energies at which radiation is produced, by discontinuities at which inflexions towards the negative direction occur, while critical electron energies at which ionization is produced disclose themselves by discontinuities at which inflexions towards the positive direction occur.

In the arrangement of electric fields for obtaining inelastic collision curves the gauzes D and C were maintained at the

same potential and a small difference of potential (1 volt or less) tending to prevent electrons from reaching the level of B was applied between C and B. Any electrons which reached this level in spite of the opposing potential difference, and which passed through the spaces of the gauze, were driven back on to the upper surface of this gauze by a difference of potential applied between A and B. A sensitive galvanometer included in the circuit between C and B therefore gave a measure of the electron current which reached the gauze B, and another galvanometer included in the circuit between F and D measured the thermionic emission from the filament.

Fig. 3.—R curves.



The curves given in figs. 3, 4, and 5 illustrate the indications of critical electron energies which were obtained by these methods. The curves shown in fig. 3 were obtained with the R arrangement of electric fields. They indicate three critical electron energies at which different types of collision occur between electrons and hydrogen atoms or molecules, which result in the production of radiation. The mean values of these critical points, taken from a large number of observations at pressures ranging from 0.002 mm. to 1 mm., are 10.2 volts, 11.9 volts, and 26.1 volts. Some

of the radiation curves suggested the existence of another critical electron energy for the production of radiation at about 12.5 volts, but the most conclusive evidence on this point was obtained from the (I—R) curves. The first radiation bend in fig. 3 is at 10.7 volts. This is because the corrections for the critical points which are indicated in this figure were found not to be the same, the lower critical point requiring a correction 0.4 volt smaller than the second critical point. Hence the voltage interval between these two corrected radiation values is not accurately represented by the interval between the two bends in the observed current-voltage curves. The electron energies marked as abscissæ in fig. 3 are those obtained by the application of the correction which was found for the second critical point to all the potential differences applied between F and D (fig. 2), so that the lower critical voltage appears too high in the curve.

The appropriate corrections to add to the measured voltages for investigations when the R and (I—R) arrangements of fields were employed was found by the "effect correction method" which the authors used in the case of neon\*. It was determined by controlling, by means of a retarding potential difference  $V_1$ , the number of electrons which were allowed to pass into the space between D and C (fig. 2), where the potential difference  $V_2$  which was applied was sufficient to allow them to acquire the necessary energy for making collisions of the type under investigation, and by finding the maximum value of  $V_1$  which would allow of the passage of a sufficient number of electrons to give a detectable indication of the effects of the collisions in as nearly as possible the arrangement of fields employed in obtaining the curve for which the correction was required. This maximum value of  $V_1$  is the amount which has to be added to the measured differences of potential in the actual series of observations. The fact that the maximum value of  $V_1$  (opposing electrons) at which a measurable photo-electric effect could be obtained, when the potential difference  $V_2$  enabled the electrons to acquire energy in excess of about 11.9 volts, was larger than when the electrons were only able to acquire energy between 10.2 volts and 11.9 volts, indicates that a smaller number of electrons is necessary to produce a measurable photo-electric current if their energy exceeds 11.9 volts than if their energy is smaller than this amount. This, in itself, is evidence in support of the

\* Proc. Roy. Soc. A, xcvi. p. 124 (1920).

genuineness of 11.9 volts as a critical energy stage, but in order to be quite sure that the bend in the radiation curve at 11.9 volts is not to be attributed to some peculiarity of the velocity distribution curve, the following procedure was adopted:—A series of observations was taken with the fields arranged for an R curve, and the “effect correction” was determined. A series of readings was then taken of the total thermionic current between F and D (fig. 2) for a series of values of  $V_1$  arranged so as to oppose electrons from the filament. From these two sets of observations the values of the ratio of the photo-electric current to the corresponding effective thermionic current were calculated, using the results of the effect correction determination as the criterion for deciding which values of the thermionic current and of the photo-electric current are corresponding. The values of this ratio were plotted against the values of the electron energy deduced from the R series of observations, and it was found that this ratio increased steadily up to between 11.5 volts and 12 volts, after which it increased much more rapidly, thus showing that there is really a critical energy value in this region. The ratio curve had the same form whether the effect correction used was the one corresponding to the lowest, or the one corresponding to the second, of the critical points in the R curve, although, as might be expected, the position of the bend in the curve varied slightly according to which correction was used.

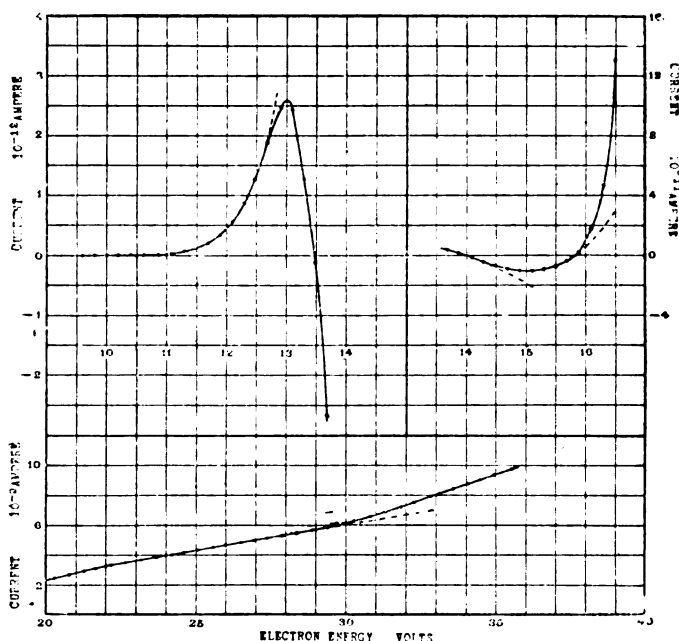
The determination by the effect correction method of the appropriate correction to apply in the case of the higher critical points, *e.g.*, that occurring at 26.1 volts in the radiation curve in fig. 3, and the ionization point shown at 29.4 volts in fig. 4 (see below), is complicated by the presence of the effects which occur at the lower energy stages. In these cases, therefore, the values have been corrected by the application of the same correction as was found necessary at the 11.9 volts and the 15.9 volts stages, for, as will be seen later, it seems probable that the higher critical values are connected with the same system as the 11.9 volts and the 15.9 volts values.

Fig. 4, which shows curves taken with the (I – R) arrangement of electric fields, confirms the suggestion of the existence of a critical energy value for the production of radiation at about 12.6 volts, and shows in addition four ionization points. The mean values of these ionization points, deduced from many series of observations, are:—10.5 volts, 13.6 volts, 15.9 volts, and 29.4 volts. As in the case of the 10.2 volts radiation point, the correction for the

10.5 volts and the 13.6 volts ionization stages was found to be 0.4 volt lower than the correction for the 15.9 volts stage, so that the interval between the ionization points in fig. 4 is not accurately represented in the curves, the two lower ones appearing to be too high. In many of the (I-R) curves no indication of the existence of an ionization energy at 13.6 volts was obtained, presumably because the amount of

Fig. 4.—(I-R) curves.

Two upper curves at 0.048 mm. pressure; lower curve at 0.180 mm. pressure.



ionization which is produced at this stage is very small, and, in the presence of the photo-electric current produced by the radiation, is only detectable for certain arrangements of the electric fields (*e. g.*, with a large value of  $V_2$  tending to drive positive ions towards the collecting electrode).

In view of the fact that the curves in fig. 3 indicate the existence of two critical radiation stages below 12.6 volts, it is interesting to note that in the (I-R) curves 12.6 volts is the first critical radiation stage indicated, and that positive ions are detected between 10.5 volts and 12.6 volts. At



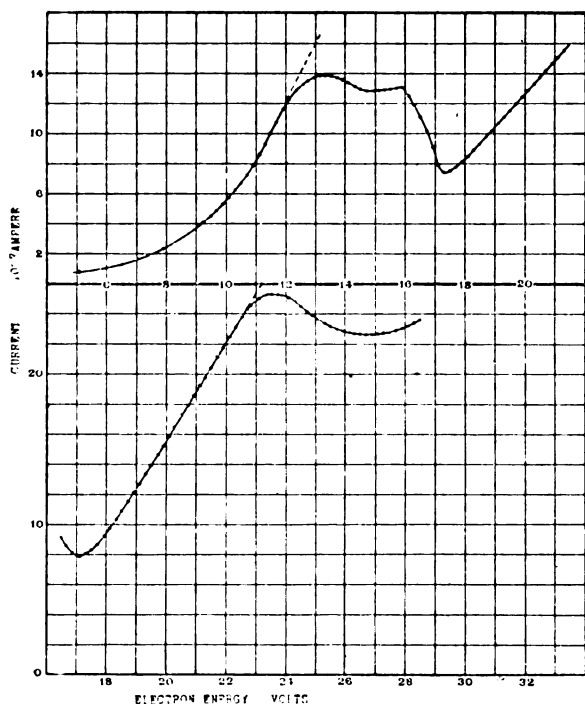
higher pressures (0.3 mm. or more) the positive current measured at this stage was very much smaller, and in some cases a small negative current was detected between 10.5 volts and 12.6 volts, in circumstances when the sharpness of the inflexion at 15.9 volts made it clear that the non-detection of positive ions could not be attributed to their failure to reach the collecting electrode. This suggests that the positive ions whose presence has been detected between 10.5 volts and 12.6 volts are not to be attributed to ionization of the hydrogen itself, but to some spurious effect, such as the production of positive ions by the electronic bombardment of the gauzes, or the ionization of a small trace of gaseous impurity. In this connexion it must be mentioned that at this stage of the research in (*I*—*R*) curves, taken in the best vacuum which we could maintain, with liquid air on and the diffusion pump working, a positive current of the same order of magnitude as that obtained with hydrogen in the apparatus began to be detected at 10.5 volts, and increased with increasing energy of the bombarding electrons. On first consideration it perhaps appears that this detection of a similar current in a "high vacuum" curve shows it to be due to electronic bombardment of the platinum gauze, but against such a conclusion must be set the fact that, in the earlier stages of the use of this apparatus, high vacuum observations of the same type showed that a very much smaller positive current was obtained for about the same electron emission, and that this effect of the bombardment of the platinum gauze did not commence before about 13 volts. As regards the second alternative, viz., ionization of a trace of impurity, the fact that the positive current was first detected at about 10.5 volts seems to point to the conclusion that, if such impurity is present, it is mercury vapour, for 10.4 volts is the value of the ionization potential for mercury. As, however, the carbon purifying tube was immersed in liquid air throughout the observations, the amount of mercury vapour present in the apparatus must have been very small. In a spectroscopic investigation of helium by one of us, the presence of the mercury line  $\lambda 5461$  was, however, detected when similar precautions had been taken to exclude mercury\*, so that the possible presence of a trace of the vapour in the present experiments cannot be ruled out on the grounds of the precautions taken to prevent its entry. Some of the (*I*—*R*) curves showed a bend in the curve at 11.9 volts, indicating that ionization increases more rapidly after this voltage is passed. This can be accounted for, if there is any system

\* A. C. Davies, Proc. Roy. Soc. A, c. p. 599 (1922).

present whose ionizing potential is less than the voltage corresponding to the radiation which is emitted at 11.9 volts, as being due to the ionization of that system by the radiation instead of simply by direct electronic collision. Olmstead † came to the conclusion that the hydrogen molecule was itself ionized without dissociation at 11.4 volts, but, as will be seen

Fig. 5.—Inelastic collision curves.

Pressure 0.179 mm.



later, the results of the spectroscopic investigation do not support such a view. The form of the ( $I - R$ ) curves between 10 volts and 13 volts will be referred to again when the origin of the various radiations is considered.

Fig. 5 shows the results obtained by the inelastic collision method. Three clear indications of inelastic collisions were found, the first at 11.9 volts, the second at 15.9 volts, and the third at 22.8 volts, and the definiteness of the bends in the curves at these stages must indicate that these three critical

† *Loc. cit.*

values are connected with encounters between electrons and hydrogen molecules. If dissociation of the hydrogen molecules could be produced by their encounters with electrons having 3.5 volts energy (Langmuir's value for the work of dissociation of the hydrogen molecule), the inelastic collision curves would be expected to show a decrease in the number of electrons reaching the gauze B at this value of the electron energy. Curves of the results obtained with small electron energies indicate, however, that dissociation by such low voltage electrons does not take place. By plotting the graph of the ratio of the current reaching the gauze B to the total thermionic emission, against the values of the electron energy, it was found that this ratio increased very considerably as the energy of the electrons was increased from about 8 volts to 10 volts. A possible explanation of this is that the hydrogen molecules have an affinity for electrons, and that those electrons which have less energy than that corresponding to a fall through about 8 volts tend to be captured by molecules, the resulting ions being more readily stopped by a small retarding difference of potential than are the free electrons.

By varying the magnitude of the potential difference  $V_3$  opposing the electrons, and by various modifications of the method, attempts were made to obtain, in curves of this type, an indication of the existence of two critical energy values as close as 11.9 volts and 12.6 volts, but none of these attempts were completely successful. This was probably due to the fact that the range of energies among the bombarding electrons was greater than the difference between 12.6 volts and 11.9 volts. It seems possible, however, that the fact that the flattening of the curve, which commenced at 11.9 volts, generally extended over a longer voltage region than the steep drop in the curve, which commenced at 15.9 volts, is to be attributed to there being two inelastic collision points fairly close together near 11.9 volts and only one at 15.9 volts. The flattening of the curve which commenced at 22.8 volts generally extended to about 27 volts, however small  $V_3$  was made, and no indication of another fall in the current at 26.1 volts, or at 29.4 volts, was obtained. In fact at 29.4 volts the current generally began to increase more rapidly than before with increasing voltage. The curves which the authors obtained in hydrogen by the inelastic collision method are very similar to those obtained by Mohler and Foote in the same gas\*. These investigators

\* F. L. Mohler and P. D. Foote, Sci. Papers, Bur. of Stan. 400, p. 669 (1920).

obtained a very definite bend in their curves in the neighbourhood of 21–22 volts\*, and they interpreted this bend as being a multiple effect due to the occurrence of two inelastic collisions of a lower energy value, though they state that the possibility of the bend being due to a new type of inelastic collision is not excluded by their work. The authors think that the results which they themselves obtained cannot be accounted for by multiple collisions, for the steepness of the drop in the current at 15.9 volts shows that a very considerable proportion of the bombarding electrons make collisions of the 15.9 volts type, and this being the case it seems improbable that when the electron energy is increased the electrons cease to make collisions of the 15.9 volts type and make instead two successive collisions of lower energy value. The authors therefore take the view that the bend in the curve at 22.8 volts indicates the occurrence of a new type of inelastic collision, though it is possible that the extent of the fall in the current over such a considerable voltage region may be accounted for by some of the electrons making two collisions of the 11.9 volts type or of the 12.6 volts type, or one of each of these types. That this possible multiple collision effect is not the main factor is evidenced by the fact that the  $R$  and  $(I - R)$  curves do not show an increased rate of production of radiation or of ionization at 22.8 volts. The absence of such an increased production of radiation or of ionization at a stage where undoubtedly an inelastic collision is occurring can only be accounted for on the supposition that the results of the new type of collision are of the same kind as the results of the last preceding type of inelastic collision, *i. e.*, in this case, that they are the same as those occurring at the 15.9 volts collision at which ionization is known to take place. Moreover, it must be the same system which is being ionized at the two critical points, but being ionized in a different way in the two cases. It is clear that the two values are to be attributed to electronic-molecular encounters because of their prominence in the inelastic collision curves, and it is possible that at one stage the process  $H_2 \rightarrow H_2^+ + \text{electron}$  takes place, while at the other the process  $H_2 \rightarrow H + H^+ + \text{electron}$  occurs, for then no increase in the number of positive charges per collision would result from the change. The value 22.8 volts is in fair agreement with that which Pauli has recently deduced, on theoretical grounds, as the voltage at which the process  $H_2 \rightarrow H_2^+ + \text{electron}$  might be expected to occur. The value which he actually gave was 23.7 volts, but this

\* Mohler, Foote, and Kurth, in the *Phys. Rev.* xix. p. 414 (1922), give this point as 22.3 volts.

involved the use of an experimental value of Franck's which the latter has since found should be reduced by 0.8 volt, so that Pauli's value becomes 22.9 volts. As will be seen later, the spectroscopic evidence indicates that the process of ionization of the molecule which occurs at 15.9 volts must be of the type  $H_2 \rightarrow H + H^+ + \text{electron}$ , because of the appearance of Balmer series lines in the spectrum at this voltage, so that the results of this investigation may be said to provide some experimental confirmation of Pauli's views.

The smallness of the effects occurring at 10.2 volts and at 13.6 volts in the R and (I-R) curves, combined with the absence of bends at these points in the inelastic collision curve, suggests that these critical values are to be attributed to collisions between electrons and hydrogen atoms and not to electronic-molecular encounters. A small proportion of atomic hydrogen might be expected to be present in the near neighbourhood of the filament, caused by temperature dissociation, but it would not be expected that the collisions of the hydrogen atoms with electrons would be sufficiently numerous to cause an appreciable reduction in the number of electrons reaching B in an inelastic collision curve, although the effects of the collisions (radiation or ionization) might be detectable if no other radiation or ionization were present. These two critical energy values are therefore taken to be the radiation and ionization voltages respectively, of the hydrogen atom; the values are in good agreement with those deduced from Bohr's theory.

With regard to the critical values which have been found at 26.1 volts and at 29.4 volts, the magnitude of the effects occurring at these stages, compared with the magnitude of the previously existing effects, must be taken to indicate that these values are to be associated with electronic-molecular encounters, even though no indication of inelastic collisions is found at these voltages in inelastic collision curves. The absence of such indications is probably to be explained by the fact that, as these energy values are approached, the number of ways in which the bombarding electrons may lose energy is so considerable that many electrons are already being prevented from reaching B, so that a change in the type of collision occurring does not result in a definite bend in the curve.

The only way in which the increased production of ionization at 29.4 volts can be accounted for is by supposing that two electrons are removed from the molecule at each inelastic collision. As it is inconceivable that the system  $H_2^{++}$  can exist alone, we are forced to the conclusion that 29.4 volts

corresponds to the work of dissociation of the molecule into two atoms and the ionization of both atoms. This conclusion is supported by the fact that the difference between 29.4 volts and 15.9 volts ( $=13.5$  volts) agrees with the directly determined value of the ionization potential of the hydrogen atom. The energy required to dissociate the molecule must thus correspond to 29.4 volts  $- 2 \times 13.5$  volts  $= 2.4$  volts. This value does not agree with the value determined by Langmuir, but is in fair agreement with the value recently obtained by Olmstead. It will be noticed that 2.4 volts is the difference between two of the observed radiation energies, namely, 10.2 volts and 12.6 volts, which suggests that 12.6 volts corresponds to the dissociation of a molecule into atoms and the excitation of one atom. Evidence on this point is given by the experiments to be described in the next section.

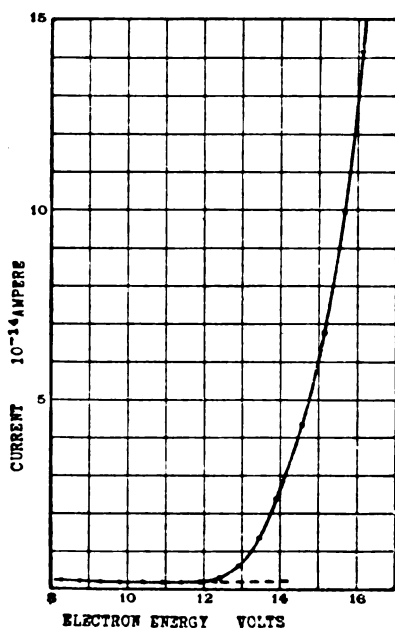
*Investigation of the Origin of the Radiations.*

The method by which this investigation was performed has already been briefly indicated. In order to insure that radiation was produced only in the space between K and L (fig. 2), the electrons from H were completely turned back in this space. The radiation produced in this space would, of course, act photo-electrically on all the negatively charged gauzes, and care had to be taken that photo-electrons so liberated were not able to acquire sufficient energy to enable them to give rise to radiation on collision with gas molecules in a region where such radiation could illuminate A or B directly. The fields  $V_7$ ,  $V_8$ , and  $V_2$  were therefore all small;  $V_7$  was about 3 volts opposing positive ions, while  $V_8$  was about 4 volts tending to prevent electrons from reaching D.  $V_2$  was about 2 volts and was in a direction accelerating electrons from C to D.  $V_3$  was larger than  $(V_6 - V_7 + V_8 + V_2)$ , the potential difference accelerating positive ions knocked out of the gauze K, and so prevented any positive ions from reaching the collecting electrode.  $V_4$  was made smaller than  $V_3$ , with the gauze B positive to the collecting electrode, *i. e.*, opposite in direction to  $V_3$ . The photo-electric effect of radiation would therefore cause electrons to leave A and a positive current to be measured. If any electrons were knocked out of the gauze C by the positive ions turned back in the  $V_3$  space, these electrons would be enabled, by means of the potential difference  $V_3$ , to acquire sufficient energy to produce radiation. As, however,  $V_4$  was only about 2 volts, these electrons would be able to reach A in spite of having

made collisions, and would give a negative current which would inevitably be larger than the positive current resulting from any radiation which they produced. The detection of a positive current with such an arrangement must therefore indicate that radiation produced in the space between the gauzes K and L has been passed on by the processes of absorption and re-emission by the gas. With hydrogen in the apparatus it was found that a positive current commenced when the electron energy was about 12 volts (see fig. 6), and

Fig. 6.—Radiation from side filament.

Pressure 0.094 mm.



that this positive current increased steadily with increase of the energy of the electrons. The magnitude of the photoelectric current measured at 13 volts indicated that the amount of radiation which passed round was about 1 part in 7000 of that produced in the side tube, an amount which is considerably more than could possibly be accounted for by reflexion.

Many series of observations of the current to the collecting electrode for gradually increasing electron energies were taken, and the resulting curves when plotted showed only the one bend at 12 volts, so that it seems probable that only one of the various types of radiation which are produced is capable of being handed on by the processes of absorption and re-emission. Even when the side filament was heated to the limit of safety no photo-electric effect was ever obtained in the main tube for values of the electron energy less than about 12 volts. Hence it must be the radiation which is produced at the 11.9 volts critical stage which can be passed on in this way. Radiation which comes round from the side tube must be produced by the excitation of a molecule without dissociation, so that the effect occurring at the 11.9 volts critical stage is evidently the genuine excitation of the molecule and the production of true molecular radiation. The radiation emitted at this stage is thus connected by the quantum relation with the critical voltage 11.9, and it would therefore be able to ionize mercury vapour (ionizing potential 10.4 volts) if this were present, as has been suggested. The sharp inflexion towards the negative direction at 12.6 volts in the (I-R) curves from the lower filament (see fig. 4) must indicate that the radiation produced at 12.6 volts, unlike that produced at 11.9 volts, is not able to ionize the gaseous impurity whose ionizing potential is about 10.5 volts. This supports the conclusion drawn from the radiation curves from the side filament, that the radiation produced at 12.6 volts does not correspond to the genuine excitation of the molecule, and, moreover, it affords strong confirmation of the suggestion that dissociation of the molecule into atoms, and atomic excitation of the 10.2 volts type, occurs at this stage, for radiation corresponding to only 10.2 volts would be unable to ionize a substance whose ionizing potential was 10.5 volts, and its effect would therefore appear in the curve as a radiation (or negative) current, and not as an ionization (or positive) current.

With regard to the critical electron energy for the production of radiation which was indicated in the R curves from the lower filament at 26.1 volts (fig. 3), no corresponding increased production of photo-electric current was found at the same stage in the radiation curve from the side filament, so that we are led to the conclusion that the process which occurs at this voltage results in an increase of atomic radiation and not in an increase of true molecular radiation. It seems probable that the process which occurs is the



following :—  $\text{H}_2 \rightarrow \text{H}^+ + \text{electron} + \text{H}^{(\text{excited})}$ , which would require  $(2.4 + 13.5 + 10.2)$  volts = 26.1 volts.

### *Results of the Spectroscopic Investigation.*

For the purposes of the present paper it is sufficient to consider the results of the spectroscopic investigation simply in so far as they throw light on the various ionization and excitation stages already referred to. The complete account of the spectroscopic investigation must be deferred to another paper. It may be stated at once that it was not found possible to excite the secondary spectrum lines at one voltage and the lines of the Balmer series at another voltage. Moreover, in no circumstances were any lines observed below the ionization potential 15.9 volts, either with or without the magnetic field to concentrate the luminosity, though the Balmer series lines and the brighter lines of the secondary spectrum were frequently observed within a few tenths of a volt of this value. If ionization of the hydrogen molecule occurred at 11.9 volts (or at 11.4 volts as Olmstead suggests) it would be expected that some, at any rate, of the secondary spectrum lines could be obtained at voltages slightly higher than this. Therefore the absence of lines may be taken as evidence that no such ionization does occur.

The spectrum of the luminosity obtained in the form of apparatus indicated in fig. 1 differed from the spectrum of that obtained in the tungsten filament apparatus with the movable anode, in that many more lines of the secondary spectrum were visible in the former than in the latter, and that altogether the secondary spectrum was very much brighter in relation to the Balmer lines in the former case than in the latter. This is doubtless to be attributed to the occurrence of a relatively greater amount of temperature dissociation of the hydrogen in the case of the tungsten filament apparatus than when the lower temperature coated platinum filament was employed. Using the apparatus indicated in fig. 1 it was found that on reducing the E.M.F. after having once obtained a bright glow, the brighter secondary spectrum lines could be seen after the Balmer series lines  $\text{H}\alpha$  and  $\text{H}\beta$  had faded out, though once these lines had ceased to be visible no further fall of potential difference between the electrodes accompanied the decrease of current until all the secondary spectrum lines had disappeared. It is therefore evident that increase of current density enhances

the Balmer series lines relatively to the secondary spectrum \*, but that in normal molecular hydrogen the lines of the Balmer series and of the secondary spectrum are excited at the same electron energy, namely that equivalent to 15.9 volts. Thus the ionization process which occurs at this voltage must involve the dissociation of the molecule into atoms, and the ionization of one of these atoms. It seems probable that the enhancement of the Balmer series lines at the greater current densities is a consequence of the rise of temperature of the gas which results from the increased current through it.

A definite blue glow could be seen in the discharge tube even when no lines were visible. This blue glow could be produced at lower voltages than were required to obtain the Balmer lines or the secondary spectrum lines, and its spectrum was found to be a continuous one extending from the yellow right across to the violet limit of the visible region. The appearance of lines in the spectroscope as the voltage across the discharge tube was raised was accompanied by the presence of a distinct pinkness in the glow, and whenever the glow showed traces of this pinkness the brighter secondary spectrum lines could be distinguished through the spectroscope. By using a retarding difference of potential of a few volts between G and H (fig. 1) a bright column of blue glow could be obtained extending right across the space between these two gauzes with traces of pinkness just in the vicinity of the gauzes. The spectrum of the luminosity could then be seen to consist of the continuous spectrum from the yellow to the violet with faint traces of lines just at the top and bottom of the field of view. With the glow in this condition it required only a small increase in the applied potential difference between F and G to cause the luminosity to change suddenly to a bright pinkish column extending the whole way between G and H, whose spectrum showed most of the secondary lines together with  $H\alpha$  and  $H\beta$ . By using a large retarding difference of potential between G and H, a stage could be obtained when, with the magnetic field on, the luminosity consisted of a short concentrated column just below G, with a distinctly blue tip at its lower end, and an outer sheath of pink glow around the part nearest G. Increasing the potential difference between F and G would then cause the pink sheath to extend downwards and shoot

\* This effect has been observed by R. W. Wood (Phil. Mag. xlv. p. 538, 1922), in his investigations of the hydrogen spectrum in long vacuum tubes.

through the blue tip until it ultimately extended the whole way. As the voltage across the tube was reduced beyond the 15.9 volts stage, the blue glow remained plainly visible, though it gradually grew fainter until ultimately it could only be detected at the surface of the gauze. It could generally be seen at lower voltages in the absence of the magnetic field, and the lowest voltage at which it was definitely observed in the present investigation was 13.5 volts, though the gradual manner of its disappearance suggested that this was not necessarily a limiting value. Its agreement with the ionizing potential for the atom appears to be fortuitous, for no trace of the Balmer series lines could be seen in the blue glow even when it was at its brightest. Moreover, with this apparatus with its low temperature source of electrons, no ionization commencing at 13.5 volts was detected. The authors think it probable that the true limit for the production of the blue glow is at 12.6 volts, the stage at which they have concluded that dissociation of the hydrogen molecule into atoms and the simultaneous excitation of one of each pair of atoms occurs, for it seems not improbable that a continuous spectrum would arise from the formation of molecules by the combining together of neutral atoms, and these would be produced for the first time at 12.6 volts. If diatomic molecules alone were formed it might be expected that the long wave-length limit of the resulting continuous spectrum would correspond to the energy of dissociation of the normal molecule, which the present research has indicated as being 2.4 volts. Although the exact determination of the long wave-length limit of the continuous spectrum of the blue glow could not be performed with a high degree of accuracy, there can be no doubt that the spectrum extended on the red side well beyond the wave-length corresponding to 2.4 volts, so that it is possible that part, at any rate, of this continuous spectrum is to be attributed to combinations resulting in the formation of some other system whose dissociation energy is less than that of  $H_2$ , possibly the system  $H_3$ .

The spectrum of the luminosity produced in the discharge tube was examined visually up to exciting voltages of about 45, but no evidence was obtained that fresh lines made their appearance at higher voltages, or that any lines already present disappeared as the voltage was increased beyond the stage at which a bright pinkish glow was first obtained.

This part of the investigation may therefore be said to have shown that ionized atoms are produced at the ionization stage at 15.9 volts, so that the process of ionization then

occurring must be  $H_2 \rightarrow H + H^+ + \text{electron}$ . If at 22·8 volts ionization occurs by the process  $H_2 \rightarrow H_2^+ + \text{electron}$ , the question arises as to whether new lines should be expected to make their appearance. Pauli thinks that the system  $H_2^+$  ultimately breaks up into  $H + H^+$  with an emission of radiation corresponding to the difference in the energies of the two systems, which would lie outside the visible region of the spectrum. If such a breaking up of the system  $H_2^+$  occurs, the final products of the ionization are the same as at 15·9 volts, so that recombination would not be expected to give rise to additional lines. Unless the system  $H_2^{++}$  can exist alone, which is very unlikely, no new lines are to be expected to make their appearance at 29·4 volts when the double ionization occurs.

It is perhaps worthy of mention that in photographs of the spectrum of the luminosity taken at 23 volts, the following lines of Group II, of Fulcher's classification were among those present:  $\lambda\lambda$  5916·8, 5931·6, 5938·9, and 6028·2. The lines  $\lambda\lambda$  5916·8 and 6028·2 were placed by Fulcher in both groups, and their classification is therefore doubtful, but the other two lines belong definitely to Group II. The present observations therefore differ in this respect from those of Duffendack, for the latter did not observe any of the Group II. lines except those of doubtful classification, even with voltages as great as 40. The Fulcher Group II. includes those lines at the red end of the spectrum which Dutour found showed a Zeeman effect. Of the other lines which show the Zeeman effect several in the region  $\lambda$  4660– $\lambda$  4800 are present on our plates, namely,  $\lambda\lambda$  4723·0, 4719·0, 4709·5, 4692·0, and 4673·1.

### Summary of Principal Results.

The various lines of investigation have indicated that the critical energy values given below correspond to the following processes:—

Volts.		
10·2...	Atomic excitation .....	$H \rightarrow H^{(\text{excited})}$ .
11·9...	Molecular excitation .....	$H_2 \rightarrow H_2^{(\text{excited})}$ .
12·6...	Dissociation + atomic excitation .....	$H_2 \rightarrow H + H^{(\text{excited})}$ .
13·5...	Atomic ionization .....	$H \rightarrow H^+ + \text{electron}$ .
15·9...	Dissociation + atomic ionization of one atom .....	$H_2 \rightarrow H + H^+ + \text{electron}$ .
22·8...	Molecular ionization .....	$H_2 \rightarrow H_2^+ + \text{electron}$ .
26·1...	Dissociation + atomic ionization + atomic excitation .....	$H_2 \rightarrow H^+ + \text{electron} + H^{(\text{excited})}$ .
29·4...	Dissociation + ionization of both atoms ...	$H_2 \rightarrow 2H^+ + 2 \text{ electrons}$ .

The results of the present experiments, while agreeing with those of the recent experiments of Olmstead with regard to the interpretation of the effects found to occur at the following voltages: 10.2, 12.6, 13.5, and 15.9 (Olmstead's values, 10.1, 12.9, 13.6, 16.0), differ from his results in regard to the critical energy stages found between 10.2 volts and 12.6 volts. Olmstead concluded that ionization of the hydrogen molecule occurs at 11.5 volts, and that the excitation of the hydrogen atom to the emission of the second line of the Lyman series occurs at 12.2 volts, whereas the present investigation has indicated only one critical energy value in this region, namely, 11.9 volts, at which it was found that radiation was produced from the molecule. This value is in agreement with the recent work of Mohler, Foote, and Kurth, who have deduced from their inelastic collision curves that there is a resonance potential at 11.8 volts, which they attribute to normal hydrogen.

The present experiments have established the existence of a genuine molecular radiation as distinct from a radiation produced by electronic-molecular encounters at which dissociation and atomic excitation occur. They have also provided a certain amount of experimental evidence in support of Pauli's suggestion that the production of positively charged hydrogen molecules requires energy equivalent to about 23 volts.

On the spectroscopic side the results of the experiments are in general agreement with those of Duffendack, except for the observation of certain lines of Group II. of Fulcher's classification, which were not detected by Duffendack at similar voltages. In addition, the experiments have shown that a visible continuous spectrum of hydrogen can be produced in the absence of the Balmer series lines and the lines of the secondary spectrum, and it is concluded that this continuous spectrum arises from the formation of molecules ( $H_2$ , or possibly  $H_3$ ) by the combination of neutral atoms.

The authors are indebted to the Radio Research Board of the Department of Scientific and Industrial Research for the means of purchasing some of the apparatus used in this investigation.

XCV. *Absorption Measurements of the Change of Wave-Length accompanying the Scattering of X-Rays.* By ARTHUR H. COMPTON, *Wayman Crow Professor of Physics, Washington University, Saint Louis* \*.

IN some recent papers † the writer has described spectroscopic experiments which have shown that when the characteristic X-rays from molybdenum are scattered by graphite, the wave-length of the X-rays is increased. While these spectroscopic investigations have been made for only two wave-lengths,  $\cdot 708$  and  $\cdot 630$  Å., a quantum theory of the phenomenon has been developed ‡ which predicts that a similar change in wave-length should occur whatever the wave-length of the primary beam. Absorption measurements on scattered  $\gamma$ -rays have indicated a change in wave-length of about the theoretical amount §, but interferometer measurements on light scattered by paraffin have failed to show any effect of this character ||. Apparently, therefore, the change in wave-length due to scattering depends in some way upon the wave-length of the primary radiation used. The present experiments, in which the change in wave-length was measured by an absorption method, have as their primary object to test the theory over a wider range of wave-lengths, and for a greater variety of scattering materials than could be done conveniently by the spectroscopic method.

The quantum theory of this change in wave-length is based upon the hypothesis that each quantum of primary X-rays is scattered by an individual electron. If the frequency of the incident quantum is  $\nu_0$ , its energy is  $h\nu_0$ , and its momentum is  $h\nu_0/c$ , where  $c$  is the velocity of light. Due to the change in direction of the quantum on scattering, its momentum is altered, resulting in a recoil of the scattering electron. Equating the momentum of recoil of the electron to the change in momentum of the quantum, we have,

$$\left\{ \frac{m\beta c}{\sqrt{1-\beta^2}} \right\}^2 = \left( \frac{h\nu_0}{c} \right)^2 + \left( \frac{h\nu_\theta}{c} \right)^2 + 2 \frac{h\nu_0}{c} \frac{h\nu_\theta}{c} \cos \theta. \quad (1)$$

\* Communicated by the Author.

† A. H. Compton, Bulletin National Research Council, xx. p. 16 (Oct. 1922); Paper before American Physical Society, April 28, 1923, Phys. Rev. June 1923; and Phys. Rev. xxii. (1923).

‡ A. H. Compton, Bull. N. R. C. xx. p. 18 (Oct. 1922); Paper before Am. Phys. Soc., Dec. 1, 1923; Phys. Rev. xxi. p. 207 (Dec. 1923) & xxi. p. 483 (May 1923). P. Debye, *Phys. Zeitschr.* xxviii. p. 161 (April 15, 1921).

§ A. H. Compton, Phil. Mag. (May 1921); Phys. Rev. xxii. (1923).

|| P. A. Ross, Science, lvii. p. 614 (1923).

*Phil. Mag.* S. 6. Vol. 46. No. 275. Nov. 1923.

3 M

Here  $\beta c$  is the velocity with which the electron recoils, and  $\nu_\theta$  is the frequency of the rays scattered at the angle  $\theta$ . But the energy of the scattered quantum is less than that of the incident quantum because of the energy spent in setting the scattering electron in motion. Thus,

$$h\nu_0 - h\nu_\theta = mc^2 \left\{ \frac{1}{\sqrt{(1-\beta^2)}} - 1 \right\} \quad . \quad . \quad . \quad (2)$$

Combining these two equations we find,

$$\nu_\theta = \nu_0 / 1 + \alpha(1 - \cos \theta), \quad . \quad . \quad . \quad (3)$$

where  $\alpha = h\nu_0 / mc^2 = h / mc\lambda_0, \quad . \quad . \quad . \quad (4)$

or  $\delta\lambda = \lambda_\theta - \lambda_0 = \gamma(1 - \cos \theta), \quad . \quad . \quad . \quad (5)$

where  $\gamma = h/mc = 0.0242 \times 10^{-8} \text{ cm.}^* \quad . \quad . \quad . \quad (6)$

Typical results of the spectrum measurements of this change in wave-length are shown in fig. 1, which represents, for slits of two different widths, the spectra of the  $K\alpha$  ray from molybdenum: (A) the primary ray, (B) as scattered by graphite at  $45^\circ$ , (C) as scattered at  $90^\circ$ , and (D) as scattered at  $135^\circ$ †. The line P is drawn in each case at the position of the primary line, and the line T at the theoretical position of the scattered line as given by equation (5). It will be noticed that, within a comparatively small probable error, the wave-length of one component of the scattered beam is exactly that predicted by this quantum theory. There remains, however, a part of the scattered beam which is unchanged in wave-length.

### *Experimental Method.*

For the measurement of the difference in absorption coefficient between the primary and the scattered ray, a balance method was employed, as is shown diagrammatically in fig. 2. Two beams of X-rays from the target X of a Coolidge tube came through separate windows in the lead box. One of them was scattered by a radiator R into an ionization chamber I, and the other went directly through a slit of variable width S into a second ionization chamber I'.

\* Since the mass of a quantum is  $h\nu/c^2 = h/\lambda c$ , the mass of a quantum of radiation of wave-length  $\gamma$  is  $h/(mc)\gamma = m$ ; i. e. a quantum of radiation of wave-length  $\gamma$  has a mass equal to that of the electron. This fact was pointed out to me by Dr. Eldridge through Prof. A. Sommerfeld.

† Cf. A. H. Compton, *Phys. Rev.* xxii. (1923).

One ionization chamber was kept at a positive and the other at a negative potential, so that with equal ionization currents

Fig. 1.

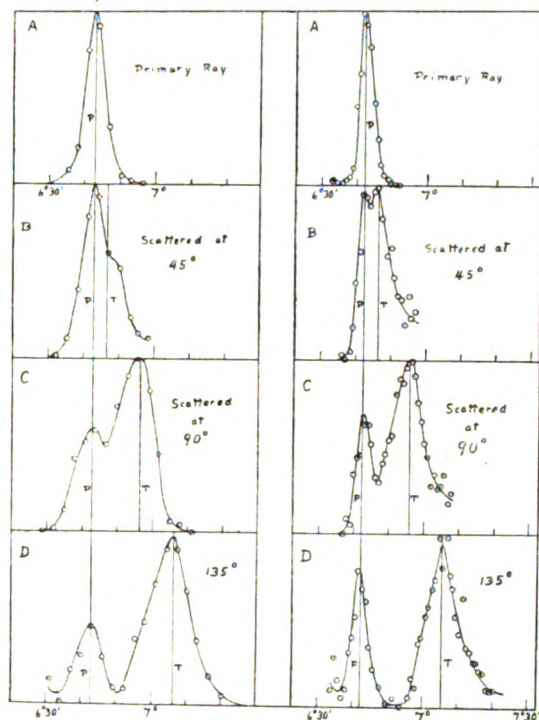
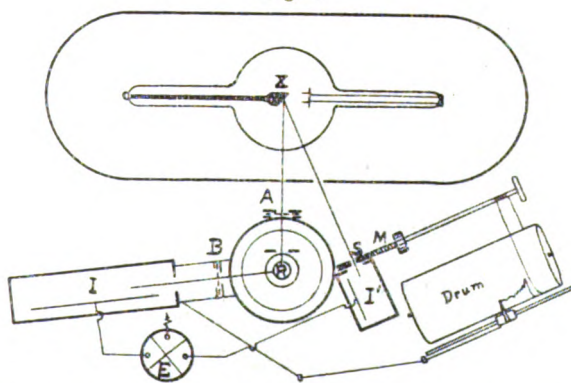


Fig. 2.



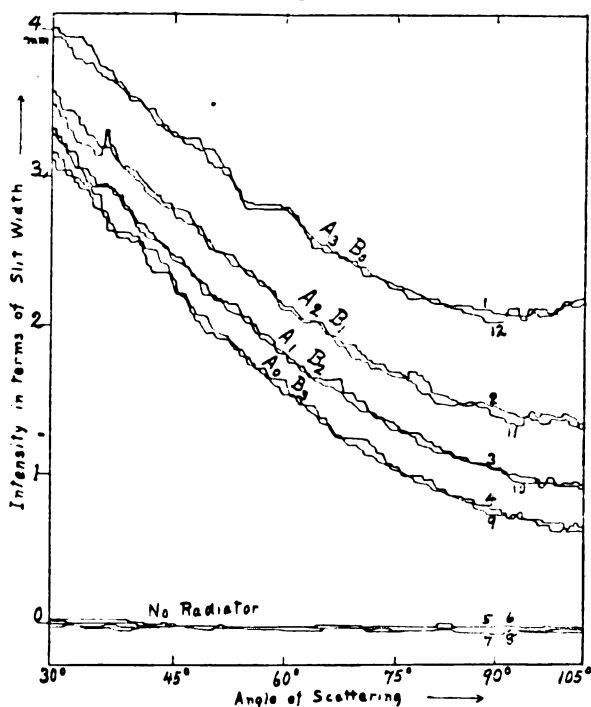
in each there was no deflexion on the electrometer E. The variable slit S was opened by a micrometer screw M.



The shaft driving this screw had wrapped about it a metal cord which was wrapped also about a drum in such a manner that the drum was rotated when the slit was opened by the micrometer screw. A recording pen moving along the drum was actuated by a metal cord fastened to the movable ionization chamber. Thus each position of the pen corresponded to a particular angle of the ionization chamber.

The chamber I was rotated through a range of angles of about  $75^\circ$  by a motor driving a worm gear. As the chamber was moving, the micrometer screw was turned so as to keep the electrometer at its zero position. In this manner a record was obtained on a sheet of paper placed around the drum showing the width of the slit for every angle of the

Fig. 3.

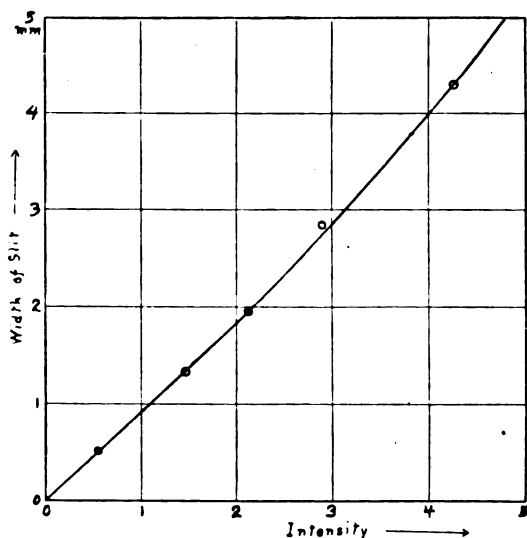


The scattering of hard X-rays by paraffin. In curve  $A_2B_1$ , 2 mm. of copper are in the path of the primary beam and 1 mm. in the path of the scattered beam, and similarly for the other curves. The fact that the intensity is greatest with the absorbing screen in the path of the primary beam shows that the wave-length of the X-rays is increased by scattering. The curves were made in the order of their numbers.

chamber I. A record of this type, copied in indian ink for reproduction, is shown in fig. 3, which represents the scattering of hard X-rays by a block of paraffin. In this figure the ordinates represent the width of the slit-opening, and the abscissæ represent the angle of the ionization chamber.

To interpret the graphs thus obtained, it was necessary to determine how the ionization in the chamber I' varied with the width of the slit. This was done by means of a sector disk made of lead which cut off a known and adjustable fraction of the primary X-ray beam. A calibration curve taken in this manner is shown in fig. 4, where the intensity

Fig. 4.



of the ionization is plotted against the width of the slit in millimetres. It will be seen that for slit-widths less than 2 mm. the calibration curve is sensibly a straight line, and that the departure from such a line is not large even for the greater widths.

The X-rays scattered into the chamber I were filtered through an absorption screen placed at A or B. It was necessary to place a similar absorption screen in the path of the rays entering I' in order that slight variations in the voltage applied to the X-ray tube should not destroy the balance between the two ionization currents. Of course,

the beam entering the chamber I was much less intense than that entering the chamber I'. This difference in intensity was balanced by making the chamber I much larger and filling it with methyl-iodide vapour.

The change in absorption coefficient, corresponding to the change in wave-length of the scattered beam, was measured by observing the relative intensity of the scattered beam when an absorbing screen was transferred from position A to position B. If  $I_p$  is the intensity of the primary beam whose wave-length is  $\lambda$  and whose absorption coefficient in the absorbing screen is  $\mu$ , and if  $S$  is the fraction of the energy of this beam which is scattered into the ionization chamber when no absorption screens are present, then the intensity of the scattered beam when a screen of thickness  $x$  is placed at A is  $I_A = I_p S e^{-\mu x}$ . If the absorption coefficient of the scattered ray is  $\mu'$ , the intensity of the scattered ray when the screen is placed at B is  $I_B = I_p S e^{-\mu' x}$ . Thus

$$\frac{I_A}{I_B} = e^{(\mu' - \mu)x}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

whence

$$\delta\mu = \mu' - \mu = \frac{1}{x} \log (I_A / I_B). \quad . \quad . \quad (8)$$

It is clear from equation (7) that if  $\mu'$  were equal to  $\mu$ ,  $I_A$  would be equal to  $I_B$ . If the absorption coefficient of each component of a complex beam of X-rays were unchanged by scattering, its intensity should therefore be unaltered by moving the absorbing screen from A to B. Hence the intensity of the whole beam should also remain unchanged. Thus any change observed in the intensity of the scattered ray when the absorption screen is shifted from position A to position B represents a change in the absorption coefficient of the component rays when the X-rays are scattered\*. The fact, which is shown clearly by fig. 3, that the intensity of the rays is greater when the screen is at A therefore means that  $\mu'$  is greater than  $\mu$ †, that is, that each component of the X-ray beam is softened during the scattering process.

\* This conclusion is strictly true only in case the fraction of the rays which is scattered from the absorber placed at A onto the radiator is the same as the fraction scattered from the absorber when placed at B into the ionization chamber. The apparatus was so designed that this condition was at least very nearly fulfilled. However, even if uncorrected, the error from this source would have been very small.

† It is by no means always true, when heterogeneous X-rays are used, that the scattered ray is softer than the primary ray. For if the radiator is of considerable thickness, the more penetrating parts of the primary beam are scattered by the whole radiator while the softer components

Knowing the absorption coefficient of the primary beam, and the change in absorption coefficient due to scattering, one can determine the wave-length of both the primary and the scattered beam. For this purpose I have employed the absorption data for different wave-lengths given by Hewlett, Richtmyer, and Duane\*.

### *Experimental Results.*

The results of these absorption measurements are collected in Table I., under the head of observer 2, and the corresponding wave-lengths are exhibited in Table II. In each case the scattering material was in the form of a cylinder, 2 cm. in diameter, with walls of such thickness that more than half of the X-rays were transmitted. The wave-length changes are very consistent with each other in every case except that of the secondary radiation from lead for the effective primary wave-length 0.14 Å. In this case the change in wave-length, especially at the small angles, is considerably greater than the theory predicts. The difficulty obviously lies in the fact that the fluorescent K radiation from lead is being excited in large amounts, and that this secondary radiation is always softer than the ray which excites it. The measurements of the scattering by the other elements for wave-lengths 0.12 and 0.13 Å. are also slightly affected by the fluorescent K radiation from the lead slits, the tendency being to make the observed change in wave-length greater at small angles and less at large angles with the primary beam, just as in the case of the scattering by lead. These fluorescent rays are not excited appreciably when the effective wave-length of the primary beam is

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are absorbed before they have penetrated very deeply. Because of this filtering process, it usually happens that the scattered ray is more penetrating than the primary. One cannot help but feel that this process may account in part for the small magnitude of the change in absorption observed by Barkla and Miss Sale (Phil. Mag. xlv. p. 758, 1923), even though they took the precaution of using thin sheets of paper as radiators. Changes in absorption due to scattering similar to those described here have been observed for  $\gamma$ -rays by Eve, Phil. Mag. viii. p. 669 (1904); R. D. Kleeman, Phil. Mag. xv. p. 638 (1908); Madsen, Phil. Mag. xvii. p. 423 (1909); D. C. H. Florance, Phil. Mag. xx. p. 921 (1910), xxvii. p. 225 (1914); J. A. Gray, Phil. Mag. xxvi. p. 611 (1913); A. H. Compton, Phil. Mag. xli. p. 749 (1921); *et al.* For X-rays the change has been observed by Sadler and Mesham, Phil. Mag. xxiv. p. 138 (1912); J. Laub, *Ann. de Phys.* xlv. p. 785 (1915); J. A. Gray, Frank. Inst. Jour. p. 643, Nov. (1920); A. H. Compton, Phys. Rev. xviii. p. 96 (1921); Nature, cviii. p. 366 (1921); and J. A. Crowthier, Phil. Mag. xlii. p. 719 (1921).

\* These data are collected in Bulletin N. R. C. no. xx. p. 32 (1922).

TABLE I.  
Mass Absorption Coefficients of Primary and Scattered X-Rays.

Radiator.	Absorber.	$\mu/\rho$ Primary.	$\delta(\mu/\rho)$ , Scattered Ray.							Observer.	
			30°.	45°.	60°.	75°.	90°.	105°.	120°.		135°.
Paraffin .....	Pb	.073	...	.027	...	...	...	...	...	.71	1
Aluminium .....	Pb	.073	...	.027	...	...	...	...	...	.43	1
Iron .....	Pb	.073	...	.037	...	...	...	.14	...	.43	1
Tin .....	Pb	.073	...	.017	...	...	...	...	...	.25	1
Lead .....	Pb	.073	...	(?)	...	...	...	...	...	.08	1
Paraffin .....	Cu	.45	.043	.08	.12	.20	.245	.32	...	...	2
Graphite .....	Cu	.46	.08	.10	.12	.19	.15	.33	...	...	2
Aluminium .....	Cu	.45	.05	.08	.13	.19	.24	.30	...	...	2
Copper .....	Cu	.59	.04	.07	.10	.15	.19	.26	...	...	2
Lead .....	Cu	.64	.21	.27	.31	.32	.33	.34	...	...	2
Paraffin .....	Cu	.76	.065	.11	.17	.26	.34	.42	.50	.59	2
Graphite .....	Cu	.76	...	.105	.16	.23	.36	.46	.52	.59	2
Aluminium .....	Cu	.76	...	.10	.14	.21	.265	.35	.42	.53	2
Copper .....	Cu	.76	...	.06	.15	.20	.23	.32	.39	...	2
Tin .....	Cu	1.03	...	.07	.12	.17	.23	.36	...	...	2
Lead .....	Cu	1.05	...	.10	.14	.14	.19	.20	...	...	2
Paraffin .....	Cu	1.74	.09	.16	.29	.405	.52	.63	...	...	2
Graphite .....	Cu	2.84	.15	.25	.33	.51	.60	.73	...	...	2
Paraffin .....	Cu	5.25	.17	.29	.50	.77	1.00	1.16	...	...	2
Paper .....	Al	.70-.90	...	...	...	...	.22	...	...	...	3
Paper .....	Al	1.15-1.83	...	...	...	...	.22	...	...	...	3
Paper .....	Al	1.90-4.42	...	...	...	...	.18	...	...	...	3
Paper .....	Al	4.8-10.3	...	...	...	...	.07	...	...	...	3

greater than  $0.15\text{\AA}$ . The fluorescent K-rays from the copper absorbing screen would also have been a source of difficulty had not the differential absorption coefficients  $\delta(\mu/\rho)$  been measured after the scattered rays had been

TABLE II.  
Change in Wave-Length Accompanying the Scattering of X-rays.

Radiator.	$\lambda$ , A.U., Primary.	$\Delta\lambda$ for Scattered Ray, Å. U.								Observer.
		30°.	45°.	60°.	75°.	90°.	105°.	120°.	135°.	
Free electron .....	All.	.003	.007	.012	.018	.024	.030	.036	.041	Theory.
Paraffin .....	.024	...	.006	...	...	...	...	...	.051	1
Aluminium .....	.024	...	.006	...	...	...	...	...	.039	1
Iron .....	.024	...	.007	...	...	.021	...	...	.029	1
Tin .....	.024	...	.004	...	...	...	...	...	.029	1
Lead .....	.024	...	...	...	...	...	...	...	.013	1
Paraffin .....	.12	.005	.010	.013	.020	.024	.031	...	...	2
Graphite .....	.12	.010	.013	.015	.021	.027	.033	...	...	2
Aluminium .....	.12	.006	.010	.015	.020	.025	.030	...	...	2
Copper .....	.13	.004	.007	.010	.014	.017	.022	...	...	2
Lead .....	.14	.016	.021	.024	.025	.025	.026	...	...	2
Paraffin .....	.15	.004	.008	.012	.018	.023	.027	.033	.039	2
Graphite .....	.15	...	.007	.012	.017	.025	.031	.034	.038	2
Aluminium .....	.15	...	.007	.010	.016	.021	.025	.028	.035	2
Copper .....	.15	...	.005	.011	.015	.017	.023	.027	...	2
Tin .....	.17	...	.004	.007	.010	.013	.020	...	...	2
Lead .....	.17	...	.005	.008	.008	.011	.012	...	...	2
Paraffin .....	.21	.004	.008	.014	.018	.023	.027	...	...	2
Paraffin .....	.25	.005	.008	.012	.017	.020	.024	...	...	2
Paraffin .....	.32	.003	.006	.010	.015	.020	.023	...	...	2
Paper .....	.30-.33	...	...	...	...	.047	...	...	...	3
Paper .....	.41-.50	...	...	...	...	.023	...	...	...	3
Paper .....	.50-.69	...	...	...	...	.015	...	...	...	3
Graphite .....	.63	...	...	...	...	.020	...	...	...	4
Graphite .....	.71	...	.003	...	...	.016	...	...	.031	4
Paper .....	.70-.90	...	...	...	...	.003	...	...	...	3

filtered through at least .5 mm. of copper. This precaution was sufficient also to eliminate the effect of the K-rays from tin when it was used as radiator.

For sake of completeness, I have included in Tables I.

and II. the results of some earlier experiments on  $\gamma$ -rays\* (Observer 1), Barkla and Sale's recent experiments on the change in absorption coefficient of soft X-rays scattered by paper† (Observer 3), and my spectrum measurements on the change of wave-length of molybdenum K-rays‡ (Observer 4). In the case of the  $\gamma$ -rays, the wave-lengths are calculated from the absorption coefficients according to the equation  $\mu/\rho = \tau/\rho + \sigma/\rho$ , where §  $\tau/\rho = 1.64 \times 10^3 \lambda^3$  and ||  $\sigma/\rho = .151/(1 + .0485/\lambda)$ . In Barkla and Sale's work, it did not seem possible to reproduce the results in successive series of experiments. I have accordingly averaged their results obtained for certain arbitrarily chosen ranges of wave-lengths, and have estimated the wave-lengths from Hewlett's data for the absorption of different wave-lengths in aluminium. The wave-length changes estimated from the spectrum measurements are the weighted mean values of the modified and the unmodified rays.

From Table II. it is apparent that in order that the scattered ray shall be changed in wave-length by the amount predicted by equation (5), X-rays of very short wave-length and radiators of low atomic number must be employed. These facts are exhibited in figs. 5 and 6. In fig. 5 is plotted the change in wave-length observed when X-rays of widely differing wave-lengths are scattered by paraffin¶. For both wave-lengths 0.024 and 0.15 Å., the observed change is very nearly that predicted by the theory (as represented by the solid curve); but the change for  $\lambda = 0.32$  Å. is slightly less, and that for  $\lambda = 0.71$  is still less than the theoretical value. Similarly in fig. 6, whereas the change in wave-length of the rays scattered by carbon is within experimental error that demanded by theory, the wave-length change for the heavier elements becomes less and less as the atomic number becomes greater. The difference here shown between the rays

\* The value of  $\mu/\rho$  for the primary  $\gamma$ -rays in lead is that of M. Ishino, Phil. Mag. xxxiii. p. 140 (1917), and for the scattered rays is from A. H. Compton, Phil. Mag. xli. p. 760 (1921).

† C. G. Barkla & Rhoda Sale, Phil. Mag. xlv. p. 748 (1923).

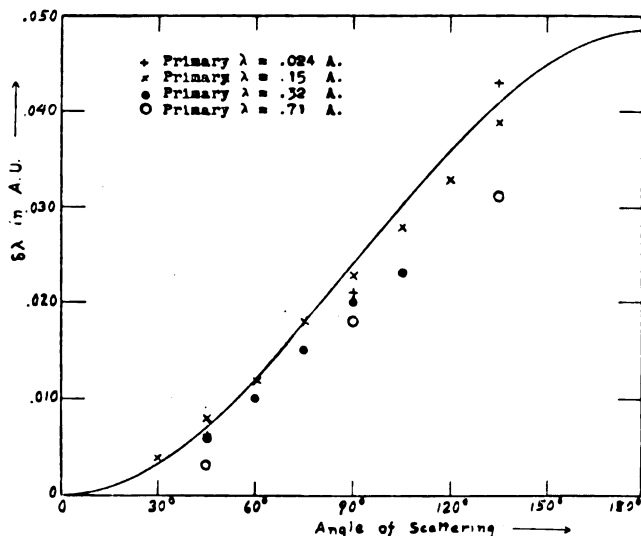
‡ For  $\lambda = 0.63$  (MoK $\beta$ -line, cf. A. H. Compton, Phys. Rev. xxi. p. 495 (1923). For  $\lambda = 0.71$  (MoK $\alpha$ -line), cf. fig. 1 of this paper.

§ A. W. Hull & Marion Rice, Phys. Rev. viii. p. 836 (1916).

|| The mass absorption due to scattering, according to the writer's quantum theory (Phys. Rev. xxi. p. 493, 1923), is  $\sigma/\rho = \sigma_0/\rho(1 + 2\alpha)$ , where  $\sigma_0/\rho$  is the mass scattering calculated on the classical theory, and has the value 0.151.

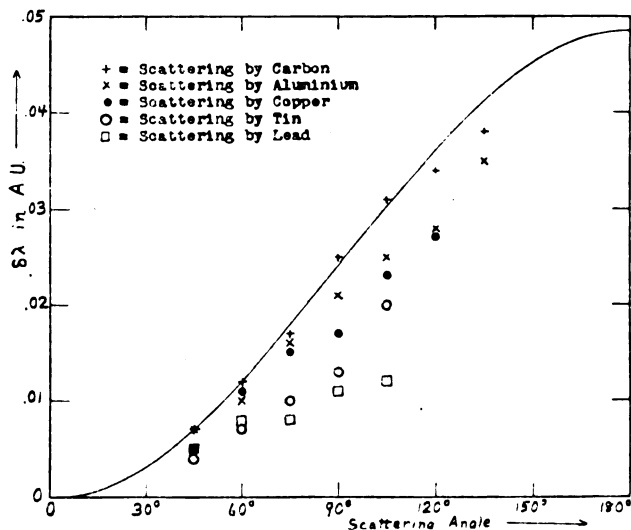
¶ In the measurements on  $\gamma$ -rays ( $\lambda = 0.024$  Å.), as plotted in fig. 5, the mean wave-length change for paraffin, aluminium, and iron is used, in order to reduce the probable experimental error. All of these elements may be considered as of low atomic number when  $\gamma$ -rays are employed.

Fig. 5.



The change in wave-length accompanying the scattering of X-rays by paraffin, when different primary wave-lengths are employed.

Fig. 6.



The change in wave-length when X-rays of wave-length  $.15-.17$  Å. are scattered by different radiators, showing a smaller change for the heavier elements.



scattered by different elements when hard X-rays are used appears also when hard  $\gamma$ -rays are employed, as is shown in Table II. In this case, however, the difference between the different elements does not become apparent for elements lighter than iron.

I do not feel that these absorption experiments are sufficiently accurate to make from them any reliable estimate of the homogeneity of the scattered X-rays. The spectrum measurements, however, such as those shown in fig. 1, indicate clearly the existence of both a *modified ray*, whose wave-length is changed by the theoretical amount, and an *unmodified ray* of unchanged wave-length. It would seem possible to explain all of the present results on the assumption that only these two rays exist in the scattered beam, but that the energy distribution between the two rays varies with the wave-length, the angle of scattering, and the atomic number of the radiator. According to this view, for short wave-lengths and low atomic numbers nearly all of the energy lies in the modified ray, while for long waves and high atomic numbers the unmodified ray has the greater energy.

These experiments therefore suggest that for such comparatively great wave-lengths as those used in optics, when the usual materials are used as radiators, the unmodified ray should predominate, and the effective change in wave-length due to scattering should be very much less than that which occurs when X-rays are scattered. This is in accord with the negative result of Ross's experiment, in which he attempted to detect a change in wave-length when light was scattered by paraffin.

### *The Limb-Effect.*

If the electrons were really free, which would correspond to atoms of zero atomic number, the present experiments suggest that the change in wave-length predicted by the theory should occur for even very long waves. J. Q. Stewart has recently presented an argument which suggests strongly that there exists about the sun a comparatively dense atmosphere of free electrons\*. If this is the case, we should expect, in addition to the spectrum lines transmitted directly through this atmosphere †, to find some scattered light from

\* J. Q. Stewart, *Nature*, cxi. p. 186 (1923); *Phys. Rev.* xxii. (1923).

† Of course, the solar lines are absorption, rather than emission lines. The change in wave-length should occur, however, in exactly the same manner. For the continuous background on either side of a dark line should be shifted toward the red, which would shift the centre of gravity of the dark line itself.

the atmosphere which would be of greater wave-length than the direct ray. Since the thickness of the atmosphere traversed is greater near the limb, the amount of scattering, and hence the effective increase in wave-length, should be greater at the limb. We might thus expect the mean wave-length of a spectrum line from the sun's limb to be slightly greater than that of the same line from the middle of the photosphere. The difference should probably be less than  $0.024 \text{ \AA.}$ , since even at the limb the direct ray would probably be responsible for a large part of the spectrum line.

An effect of exactly this character is found in the solar spectrum, and is known as the "limb effect." Dr. C. E. St. John writes me that the wave-lengths from the limb are greater than those from the centre by from  $0.004$  to about  $0.010 \text{ \AA.}$  in passing from the violet to the red. This neglects the very strong lines, which show no change in wave-length, and which presumably originate above the denser part of the electron atmosphere. The observed limb effect is thus of the right sign and of the right order of magnitude. At first sight it seems difficult to account for the fact that the red lines are shifted more than the violet. It is very possible, however, that the violet light is the more rapidly absorbed by the sun's atmosphere, so that the violet light reaching us traverses a thinner stratum of electrons. Our ignorance of the relative amount of the primary and the scattered light in the solar lines makes it impossible at present to give this explanation of the limb effect a quantitative test; but qualitatively it seems to be satisfactory.

#### *Possible Origin of the Unmodified Ray.*

Two different hypotheses suggest themselves to account for the presence of the unmodified ray. The first is that if the momentum of the light quantum is insufficient to impart to the scattering electron enough kinetic energy to eject it from the atom, the electron is held so firmly that it cannot recoil. Since in this case no energy is lost by recoil, the frequency of the scattered ray is the same as that of the incident ray. According to this view, many of the electrons in the heavier elements would be so tightly bound that they could recoil only from quanta possessing great energy, whereas for low energy or long wave-length quanta, even in the lighter elements some of the electrons would not recoil, thus giving rise to unmodified scattering. This is in accord with experiment. Quantitatively, however, the hypothesis is not so satisfactory. Thus the kinetic energy of an electron

recoiling with the impulse imparted by a molybdenum  $K\alpha$ -ray when deflected through  $135^\circ$  is greater than the critical ionizing energy (280 volts) of the K electrons in carbon. We should therefore expect that no unmodified ray should appear when these rays are scattered at  $135^\circ$  by carbon. The spectra exhibited in fig. 1, however, show that the unmodified ray is present under these conditions.

The second hypothesis is based upon the view that when interference occurs, two or more electrons must scatter the same quantum. The theory upon which equation (5) is based, however, supposed that each quantum is scattered by a single electron. The change in wave-length is proportional to  $1/m$ , where  $m$  is the mass of the body which scatters the ray. If, then, the ray is scattered simultaneously by two electrons, the change in wave-length should be  $1/2$  the maximum value, and if interference occurs between the rays scattered by a large number of electrons, as in the case of crystal reflexion, the change in wave-length should be negligible. According to the wave-theory, partial interference should always occur when more than one electron is traversed by an electromagnetic wave. Experimentally, however, we have no evidence that the rays scattered by small groups of electrons, such as those in an atom of low atomic number, interfere with each other except when the phases of the rays scattered by the individual electrons are nearly identical. This is the condition, for example, under which excess scattering of X-rays occurs. There is accordingly some justification for the assumption that an electron scatters independently only when removed from other electrons by a distance greater than some fraction of a wave-length of the incident ray. If the electrons are closer than this, they will cooperate in their scattering, and in view of their large total mass, no appreciable change in wave-length will result. This hypothesis therefore leads also to an unmodified ray which possesses greater relative energy as the wave-length of the primary ray and the atomic number of the radiator are increased.

On the latter hypothesis, there should be no change of wave-length when X-rays are regularly reflected from a crystal, or when light is reflected by the free electrons of a metallic mirror, whereas according to the former hypothesis such a change might have been anticipated. The fact that experiment seems not to show any wave-length change in these cases\* is a point in favour of the view that the

\* The test on light reflected by a mirror has been made by P. A. Ross (*loc. cit.*); that on the wave-length of reflected X-rays is being made in this laboratory.

unmodified ray results from scattering by groups instead of by single electrons.

*Summary.*

The present absorption measurements on hard X-rays, when combined with the writer's earlier measurements on  $\gamma$ -rays and his spectrum measurements on soft X-rays, show that over the range of primary wave-lengths from 0.7 to 0.024 Å., there occurs a change in wave-length during the scattering process.

For light elements and short wave-lengths the effective wave-length change is very near the theoretical value  $\delta\lambda = 0.024 (1 - \cos \theta)$ , but is less for long wave-length X-rays and for radiators composed of heavy elements.

It appears probable that in each case the scattered ray consists of two portions, an unmodified ray for which  $\delta\lambda = 0$ , and a modified ray for which  $\delta\lambda = 0.024 (1 - \cos \theta)$ . The effective wave-length change then depends upon the distribution of energy between these two rays.

Two different hypotheses are suggested to account for the existence of the unmodified ray.

The limb effect, or difference in wave-length of solar lines between the centre and the limb of the photosphere, receives a satisfactory qualitative explanation on the view that it is due to a change in wave-length as the light is scattered by an electron atmosphere around the sun.

Washington University,  
Saint Louis, U.S.A.  
June 23, 1923.

XCVI. *The Generalized Quantum Conditions.* By O. W. RICHARDSON, F.R.S., *Wheatstone Professor of Physics in the University of London* \*.

FROM a consideration of the equations of motion of an electrified particle on the general theory of relativity, Professor W. Wilson† has suggested an extension of the quantum conditions for such a particle executing a periodic motion, in the form

$$\oint (p_s + eA_s) dq_s = n_s h, \quad s = 1, 2, 3, 4, \dots \quad (1)$$

where the  $p_s$  and  $q_s$  are the Hamiltonian coordinates,  $e$  is the

\* Communicated by the Author.

† Proc. Roy. Soc. A, vol. cii. p. 478 (1922).

charge,  $A$  the four-vector potential,  $h$  Planck's constant, and the  $n_s$  integral numbers. The integrals in each case are to be extended over the period of the corresponding  $q$ . The first three equations are shown to lead to a natural account of the normal Zeeman effect, but the fourth equation is not explicitly considered in the paper. However, about the time at which Professor Wilson read his paper to the Royal Society, he informed me, in conversation, that the fourth equation could be transformed into the quite simple expression

$$-\int (T + V) dt = n_4 h, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where  $T$  is the kinetic and  $V$  the potential energy of the particle, and  $t$  the real time. This equation can readily be verified.

One might be tempted to argue from the symmetry of the equations that  $n$  should also be an integer like  $n_1$ ,  $n_2$ , and  $n_3$ , but this cannot, in general, be the case, owing to the fact that these numbers are not entirely independent of one another. This may be made clear by considering one or two simple cases.

There are several important types of motion for which the first three members of (1) reduce to the single equation

$$\int p dq = nh, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where  $n$  is an integer. If, furthermore, the motions are executed with constant energy (for example, without radiation as in the stationary states of a simple Bohr atom), we have

$$\int p dq = 2 \int T dt. \quad . \quad . \quad . \quad . \quad . \quad (4)$$

So that, for such motions,

$$2 \int T dt = nh. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

In the case of a Planck oscillator

$$\int T dt = \int V dt; \quad . \quad . \quad . \quad . \quad . \quad (6)$$

so that if the motion of a Planck oscillator is to be subject to (3)—or its equivalent (5)—and (2), we must have

$$n_4 = -n. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

In the case of a simple Bohr atom

$$T_n = \frac{1}{2} E e \left( \frac{2}{r} - \frac{1}{a_n} \right), \quad V_n = -E e / r, \quad . \quad . \quad . \quad (8)$$

where the suffix  $n$  indicates that the motion referred to is the one governed by the integer  $n$  in (3),  $E$  and  $e$  are the nuclear and electronic charges,  $r$  the instantaneous radius, and  $a_n$  the semi-major axis. In this formula the potential energy  $V_n$  is measured from an infinitely distant configuration. As this is arbitrary, it is perhaps preferable to add an arbitrary constant  $A$  to the potential energy. If this is done and equation (2) is to apply to the motion, we have

$$\int \left( A - \frac{Ee}{2a_n} \right) dt = -n_1 h,$$

$$\text{or} \quad Ee/2a_n = n_1 h \omega_n - A,$$

if  $\omega_n$  is the orbital frequency. Putting in the values of  $a_n$  and  $\omega_n$  required by condition (3), we get

$$2\pi^2 \frac{Mm}{M+m} \frac{E^2 e^2}{n^2 h^2} = \frac{n_1}{n} 4\pi^2 \frac{Mm}{M+m} \frac{E^2 e^2}{n^2 h^2} - A,$$

$M$  and  $m$  being the nuclear and electronic masses. This equation shows that  $A$  must be zero, otherwise it would depend on  $n$ . In order to satisfy the equation, it is necessary and sufficient that

$$n_1 = +n/2. \quad . \quad . \quad . \quad . \quad . \quad (9)$$

We know from the spectroscopic evidence that  $n$  can take all integral values; so that for a Bohr atom it appears that  $n_1$  can take positive semi-integral as well as integral values. This result is, however, special to the laws of force governing the motion, because we see from equation (7) that in the case of a Planck oscillator,  $n_1$  is confined to negative integral values.

Provided the velocities in the motions remain small compared with the velocity of light, the results can be generalized to central forces varying as any power of the distance by means of a theorem used by Bohr and Burgers and apparently due to Jacobi\*. According to this theorem, if the force varies as  $r^\mu$ ,

$$\int T dt = \frac{\mu+1}{2} \int V dt. \quad . \quad . \quad . \quad . \quad (10)$$

Using this to eliminate  $\int V dt$  from (2), we obtain

$$\int \left( 1 + \frac{2}{\mu+1} \right) T dt = -n_1 h,$$

\* Cf. Sommerfeld, *Atombau und Spektrallinien*, 3rd Edition, Zusatz (5), p. 666; English translation, p. 548.

which gives, in combination with (5),

$$\frac{n}{2} + \frac{n}{\mu+1} = -n_4$$

$$\text{or} \quad n_4 = -\frac{\mu+3}{2(\mu+1)}n.$$

The following table gives a series of values of  $n_4$  in terms of  $n$  for different values of the index  $\mu$  :—

$\mu \rightarrow$	$+\infty$	$+1$	$+1/2$	$0$	$-1/2$	$-1$	$-3/2$
$n_4 \rightarrow$	$-n/2$	$-n$	$-7n/6$	$-3n/2$	$-5n/2$	$+\infty$	$+3n/2$
$\mu \rightarrow$	$-5/3$	$-2$	$-3$	$-4$	$-5$	$-6$	$-\infty$
$n_4 \rightarrow$	$+n$	$+n/2$	$0$	$-n/6$	$-n/4$	$-3n/10$	$-n/2$

From this table it will be seen that for a force varying as the direct distance, as in a Planck oscillator,  $n_4 = -n_1$ ; for an inverse square law, as in a simple Bohr atom,  $n_4 = +n/2$ ; for an inverse cube law  $n_4 = 0$ , and so on. Whilst the physical interpretation of these numerical connexions is not yet clear, the occurrence of the factor  $1/2$  with the inverse square law seems suggestive in relation to the fact that the individual constituents of band spectra require half-quantum numbers for their series arrangements. It also seems possible that the fractional relations arising with the more unusual laws of force may be connected with the complex Zeeman effects which appear to be symptomatic of motions in intra-atomic fields of complicated types.

The integrals expressed in this paper are to be read as definite integrals extended over a complete period of the relevant  $q$  (or  $t$ ).

April 1923.

*Note added Sept. 2, 1923.*—It may be objected that since  $T+V$  is constant in the motions considered there is no mathematical periodicity in time of this function. There is, however, a periodicity in the physical properties of the energy. An alternative procedure suggested by W. Wilson would be to use the fourth relation to define an additional frequency.

XCVII. *The Relative Activities of Radioactive Substances in an Unchanged Primary Uranium Mineral.* By W. P. WIDDOWSON, B.A., *Scholar of Christ Church, Oxford,* and A. S. RUSSELL, M.A., *D.Sc.\**

§ 1. *Introduction.*

THE work of Boltwood † showed that in an unchanged primary uranium mineral there are about 2·2 atoms of uranium breaking up per second for one of each of its disintegration products, and that the total activity due to the actinium series is about 0·28 of that of uranium taken as unity. From this it was deduced that uranium consists of two radio-elements, Uranium I and Uranium II, in equilibrium, and the scheme to give these a place in the radioactive series, suggested by one of us ‡ was confirmed later by the experimental work of Fajans and Göhring §. To account for the 0·2 in excess of 2, Rutherford || suggested that branching occurred either at Uranium I, or Uranium II, one of these elements undergoing a dual change with the expulsion of an  $\alpha$ -particle, forming two products which give rise to the uranium and actinium series respectively. Rutherford suggested that 8 per cent. of the parent substance was transformed into the actinium series; but it may also be calculated from Boltwood's results that if the change occurs at uranium I 26 per cent. breaks up, and if at uranium II 14 per cent., to form the actinium series. Later experiments, however, notably those of Hahn and Meitner ¶, showed that the actinium series had only 3 per cent. of the activity of the radium series, and Meyer \*\* found it to be 4·2 per cent. The discrepancy is striking, and one of the objects of this work was to elucidate this point.

The relative activities of certain radio-elements of the uranium series and of the whole actinium series when in equilibrium have been evaluated from the calculated relative ionizations of the  $\alpha$ -ray bodies on various assumptions respecting the amount and the place of branching. These are given in Table I. This table includes also calculations

\* Communicated by the Authors.

† E. B. Boltwood, *Amer. Journ. Sci.* vol. xxv. p. 269 (1908).

‡ A. S. Russell, *Chem. News*, vol. cvii. p. 49 (1913).

§ K. Fajans and O. Göhring, *Phys. Zeit.* vol. xiv. p. 877 (1913).

|| Sir E. Rutherford, 'Radioactive Transformations,' p. 170 (1906).

¶ O. Hahn and L. Meitner, *Phys. Zeit.* vol. xx. p. 529 (1919).

\*\* S. Meyer, *Wien. Anzeiger*, p. 133 (1920).



made on the assumption that actinium arises from an isotope of uranium of atomic weight 239, whose activity is either 3 or 8 per cent. of that of uranium I. The calculated values are compared with those obtained by Boltwood † in his original paper, and with those given by Johnstone and Boltwood ‡ in a subsequent paper, which substantially confirm the earlier one. The latter are marked with an \*.

TABLE I.

	No branch in the Uranium series.	Branch at Uranium I.		Branch at Uranium II.		Independent isotope parent of Ac. series.		Boltwood's values.
		3 %.	8 %.	3 %.	8 %.	3 %.	8 %.	
Whole mineral Uranium	5.23	5.31	5.47	5.24	5.26	5.25	5.29	4.64, 4.73 *
Ionium Uranium	0.56	0.55	0.54	0.54	0.52	0.55	0.52	0.34
Radium Uranium	0.60	0.59	0.57	0.58	0.55	0.58	0.55	0.45, 0.49 *
Polonium Uranium	0.65	0.64	0.62	0.63	0.60	0.63	0.60	0.46
Actinium Series Uranium	...	0.145	0.39	0.143	0.38	0.17	0.42	0.28

It is seen from this table that the effect of branching in the series is, as one would expect, to alter the ratio of uranium to one of the products in the major branch, but to have a small effect only on the ratio of uranium to the total activity of the whole mineral. (This is explained by the fact that the number of ions produced by single  $\alpha$ -particles from the products of the actinium series is nearly equal to that produced by single  $\alpha$ -particles from the products of the uranium series.) Boltwood's work appears to show that *both* of these ratios are abnormal; in other words, although the assumption that branching occurs explains the lowness of such ratios as ionium to uranium, polonium to uranium, etc., it does not explain that of the whole mineral to uranium. To explain both it would appear simplest to assume in addition that the

† B. B. Boltwood, *loc. cit.*

‡ J. H. L. Johnstone and B. B. Boltwood, *Phil. Mag.* vol. xl. p. 50 (1920).

uranium used by Boltwood is more active than is to be expected. This might be explained by one of the following reasons:—

- (1) The  $\alpha$ -particles from uranium ionized relatively more than is to be expected from their range in the electro-scope used.
- (2) An  $\alpha$ -ray body not of atomic number 92 was present in his uranium.
- (3) An isotope of uranium is present which emits  $\alpha$ -rays, and initiates a disintegration series which is not completed like the radium and actinium series.
- (4) A branch series of considerable magnitude begins at radium (which is known to emit  $\beta$ -particles as well as  $\alpha$ -particles).

It cannot be argued that Boltwood failed to make quantitative separations of the individual products, because the aggregate of their separate activities is approximately that of the mineral before separation.

Of the possibilities enumerated, (1) is unlikely, (2) out of the question, (3) is possible but there is no proof at present that it is true, (4) has been definitely disposed of by Hahn and Meitner\*.

In order to throw light upon the subject, if possible, we have carefully repeated part of Boltwood's work, using the improved chemical methods that have been developed since 1906. The results obtained will now be described.

## § 2. *Methods of making Measurements.*

The  $\alpha$ -ray electro-scope used in these experiments had an ionization chamber of 10·3 cm. in diameter and 13 cm. in height. A disk of brass was attached by the rod to the gold-leaf system, and fixed so as to be in a plane parallel to that of the disk of radioactive matter, at a distance of 6 cm., the disk being carried on the removable base. This allowed the rays to give complete ionization; and the rate of collapse of the gold-leaf (after being charged to about 700 volts in the usual way, which is sufficient to give the saturation current) was found by timing the fall over a certain number of divisions on a scale in the eyepiece of a reading-microscope.

The sensitiveness of the instrument was such that 1 milligram of radioactively-pure uranium oxide ( $\text{U}_3\text{O}_8$ ) gave a net leak of 0·83 division per minute. The natural leak

\* O. Hahn and L. Meitner, *Zeit. Physik*, vol. ii. p. 60 (1920).

was about 0.78 division per minute, and was very constant, never varying beyond 0.02 or 0.03 division per minute throughout the research.

The radioactive matter was contained on copper disks 3 cm. in diameter, which for convenience of handling were supported on small stands. Films were made by grinding the substance to be measured to a very fine powder, making it into a suspension in chloroform, and painting this evenly on to a copper disk in the way recommended by McCoy. When the chloroform evaporated, an even film was left which adhered to the disk so that it could be moved about without fear of loss.

The chief difficulty in making comparative measurements of activity by measuring the ionization due to  $\alpha$ -rays is the great absorption of these rays by the material containing the active matter. This is so great that with increasing thicknesses of film a limit is reached beyond which there is no further increase of activity due to  $\alpha$ -particles.

There are three ways in general use for getting over this difficulty, each of which has disadvantages. (1) McCoy \* takes weighed films of increasing thickness and measures their activities, plots the weight against the ratio of weight to activity, and extrapolates his curve to obtain this ratio at zero weight, *i. e.* for a very thin film in which there is presumably no absorption. (2) Soddy uses the "limiting activity" method. In this method films are made of such thickness that their activity has reached its maximum. The product of the weight and the activity of such a film bears a simple relation to the activity obtained by the other methods. (3) Boltwood † and others advocate using films made of very small quantities of material. In such films the absorption is small, and for comparative measurements on similar films may be neglected. It is understood, of course, that whatever method be employed disks of one diameter only must be used throughout the series of measurements.

We employed the method (1) at first, but our experience after making many careful measurements is that it was difficult to get the good curves obtained by McCoy, and that it was not possible by extrapolation to obtain a very certain zero result. With it we obtained results for the activities of ionium, uranium, and for the whole ore which appeared to be of the right order; but we abandoned it later for method (3), which we think is the best.

In method (2) a comparatively large quantity of material

\* H. N. McCoy, *Phil. Mag.* vol. xi. p. 176 (1906).

† B. B. Boltwood, *Amer. Journ. Sci.* vol. xxv. p. 269 (1908).

is required. For the disks we used, about 100 mgs. of material was required to give maximum activity. This has the disadvantage that it is not always possible or desirable to obtain this amount of material. Nor is it possible to compare directly a very thin film, such as is obtained when polonium is deposited electrolytically, with a film of this kind.

The third method was the one eventually adopted in these experiments. Films, which were never allowed to exceed 5 mgs. in weight, were made as described above, and it was assumed in these circumstances that there was no absorption. The great drawback to this method is the accurate determination of the weight of the films. In practice the disk was weighed just before the film was applied and, to check it, just after its removal, and if there was any difference the mean of the two readings was taken. A balance was used which made it possible to weigh to the twentieth of a milligram. It was found that fairly consistent results were obtained, as is shown by the following figures :—

Weight in mgs.	Activity (div./min.).	Activity per mg.
4.50	6.60	1.47
3.95	5.86	1.485
4.75	6.93	1.46
2.70	4.01	1.49

For convenience, activities in divisions per minute will be referred to hereafter simply as activities.

### § 3. *Purification and Activity of Uranium Oxide ( $U_3O_8$ ).*

It is essential for this work to know accurately the activity of a specimen of uranium oxide ( $U_3O_8$ ), pure chemically and free from all radio-elements except its own quick-changing  $\beta$ -ray products, uranium  $X_1$ , uranium  $X_2$ , uranium  $Y$ , and uranium  $Z$ . This was obtained by the following standard procedure.

To a solution in water of a few grams of uranium nitrate, a solution containing a few milligrams of lead and bismuth nitrates was added, and hydrogen sulphide passed through the acidified solution, the precipitated sulphides being filtered off and the solution boiled. The precipitate contains proto-actinium and all the disintegration products after the radium emanation which might be present. A solution containing a few milligrams of thorium nitrate

was added to the filtrate, and the thorium precipitated from nearly neutral solution by hydrofluoric acid. This removes products of atomic numbers 90 and 89. The filtrate was boiled to expel hydrogen fluoride completely. To it was added a solution containing a few milligrams of barium chloride. The barium, precipitated by dilute sulphuric acid, carries with it products of atomic number 88.

The uranium was then precipitated with ammonia and dissolved in ammonium carbonate, filtered, the precipitate treated with nitric acid, the carbon dioxide expelled, and the uranium again precipitated with ammonia. This was repeated three times, and the yellow ammonium uranate so obtained was ignited in a crucible to uranium oxide ( $U_3O_8$ ), with which the films were made.

The original uranium salt was probably comparatively free from radioactive impurities, the above treatment making it quite so, except of course for the quick-changing products which soon grow again. The effect of the  $\beta$ -particles from these in the electroscope was just less than 2 per cent.

Its purity with regard to its formula,  $U_3O_8$ , was tested by dissolving in sulphuric acid and reducing it quantitatively by zinc amalgam, and titrating the uranous solution with  $N/20$  permanganate solution.

A specimen of purified  $U_3O_8$  lent to us by Prof. F. Soddy gave a very similar activity to our own.

A disk of this material was kept as a standard, and measured from time to time to ensure that the sensitiveness of the gold-leaf did not change during the course of the research. The extreme difference found was 0.14 div. in 17 div., which is less than 0.9 per cent.

The following results for  $U_3O_8$  were obtained:—

Weight (mgs.).	Activity.	Activity per mg.
3.25	2.74	0.845
3.55	3.02	0.852
3.15	2.60	0.827
3.275	2.66	0.812

These results give a mean activity of 0.834 per mg. Therefore 1 gram of an ore containing 38.4 per cent.  $U_3O_8$  will have an activity 320. It was found that 2 per cent. of this was due to the ionization of uranium X and uranium Y. The corrected activity is therefore **313.5**.

§ 4. *The Analysis and Activity of Pitchblende.*

The pitchblende used throughout these experiments consisted of lumps of mineral about the size of peas, which were ground up to a very fine powder. It was analysed by dissolving about half a gram in dilute nitric acid, removing the silica by filtration, the lead as sulphate, and the iron as ferric hydroxide in presence of excess of ammonium carbonate; the uranium was finally precipitated as ammonium uranate from a solution freed from carbon dioxide and estimated as  $U_3O_8$  in the usual way. A mean value of 38.4 per cent.  $U_3O_8$  was obtained from three experiments. This was checked (*a*) by estimating uranium volumetrically after the removal of iron, and (*b*) by the radium-emanation method against a carefully analysed specimen of a primary thorianite.

The following results were obtained from films of the material on the day the films were made:—

Weight (mgs.).	Activity.	Activity per mg.
4.50	6.60	1.47
3.925	5.86	1.49
4.75	6.93	1.46
2.70	4.01	1.49

The mean activity of 1.48 per mg. was found to increase, as though there had been a temporary loss of emanation in the making of the films. A fortnight later the mean activity per mg. was found to be 1.545, which did not increase further. The films were then assumed to be in the position that any loss of activity due to diffusion of emanation from them was constant. This permanent loss of emanation, due to the finely-ground state of the ore, was corrected for in the usual way. Emanation was completely expelled from an untouched portion of the finely-ground material, and its amount measured in the usual way in an emanation electroscope. The solution was sealed up for a known time, and from the quantity which had in that time been formed the total amount in equilibrium was calculated. This was found to be 4 per cent. greater than the first. 4 per cent. is consequently the amount of emanation permanently lost by diffusion. In addition to radon, radium A and radium C' alone are affected. The correction to be applied to the mineral is therefore calculated to be 1.8 per cent. The corrected activity per gram of ore is in consequence 1573. There was no trace of thorium in the mineral.

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§ 5. *Estimation and Activity of Polonium.*

Polonium may be estimated in two ways:—

- (a) By deposition from solution on to a copper disk ;
- (b) By chemical separation with bismuth.

The first was obviously, and was also found by experiment to be, the better way. In this method about 0·6 gram of pitchblende was digested with strong hydrochloric acid and filtered from undissolved silica. The solution, which was somewhat neutralized, was made up to 150 c.c., and in it a copper disk was rotated just below the surface, by an electric motor. The disk was attached to a rotating glass rod by means of Bunsen cement, which allowed it to be removed easily after the experiment. One face of the disk was highly polished, the remainder of it being coated with paraffin wax. After one and a half hours the disk was removed and a second substituted for it. This was again replaced after a similar interval, and so on till all the polonium was deposited as infinitely thin films whose activity was determined in the electroscope. This was found to take about nine hours.

The decay of these films was followed in the electroscope, and assuming the half-value period to be 136 days, the amount at the beginning was calculated back and the mean of the values taken. No readings were taken till after the first day, so as to allow any quick-changing bodies deposited to decay.

In an experiment in which the ore was taken up with sulphuric acid, no activity at all could be obtained on the disks.

Owing to the great tendency of polonium to deposit itself from solution, as shown by Boltwood, these experiments were always carried out immediately after the ore was dissolved.

*First Experiment.*

The polonium was derived from 6436 gm. of ore.

Activity after	1	5	9	33	54 days.
	133·4	128·7	125·7	110·9	101·8
Initial activity calculated back to zero .....	134·1	132·0	131·6	131·2	134·0

Giving mean of 132·6.

Activity per gram of ore is 204.

*Second Experiment.*

The polonium was derived from 6276 gm. of ore.

Activity after	1	27	46 days.
	120.7	106.4	97.8
Calculated back to start...	121.3	122.0	123.7

Giving mean of 122.3.

Activity per gram of ore is 195.

From the above figures a value of **200** was taken as the activity due to polonium.

§ 6. *Estimation and Activity of Radium.*

The activity in the mineral due to radium was estimated by precipitating it along with barium as sulphate. To a solution of the ore in hydrochloric acid, a few drops of bismuth and thorium nitrates were added and sufficient barium chloride solution to give about 100 mgs. of the sulphate. The hydroxides of uranium, bismuth, thorium, etc. were precipitated with ammonia and filtered off. This precipitate was dissolved up and reprecipitated so that any adsorbed barium chloride in the first precipitate remains in solution the second time. The ammoniacal solutions were added together and made just acid with hydrochloric acid, excess of sulphuric acid added, and the resulting barium sulphate collected, dried, weighed, and its activity determined on disks in the usual way.

It was found that the films so made gained 27 per cent. in activity in 16 hours. In order, therefore, to avoid as far as possible disturbances due to the growth of the emanation and its products in the radium, this procedure was improved so that readings might be made in a minimum time after the precipitation.

It was assumed for this purpose that when a certain amount of barium is added to a solution containing radium, the latter behaves exactly like the former in the few chemical operations through which they are put; so that if, say, 90 per cent. only of the barium present is precipitated, exactly 90 per cent. of the radium is precipitated with it. Accordingly, to the solution of the ore a known weight of barium chloride was added, and hence the corresponding weight of sulphate could be calculated. In practice 10 c.c. of a solution containing 3.978 gs. of hydrated barium chloride per 250 c.c., that is 159 mgs. in the 10 c.c., which is equivalent to 152 mgs. of the sulphate. The experiment was

then conducted as before, except that it was not necessary to reprecipitate the hydroxides, and the precipitate of barium sulphate when formed was filtered as quickly as possible at the pump, the filter paper was immediately ignited, the films made and their activity at once measured. The films were weighed later, and from their weight and activity it was calculated how much activity there was in the 152 mgs. barium sulphate, *i. e.* in the quantity of mineral taken.

In these experiments nitric acid was found to be unsatisfactory as a solvent for the mineral, because the latter contains sulphur which was oxidized by the nitric acid to give sulphate, and this of course immediately precipitated a certain amount of the barium on addition. With hydrochloric acid this difficulty did not arise, and for this specimen of pitchblende it was found to be as good a solvent as nitric acid.

#### *First Experiment.*

Weight of ore, 1.713 gm.

Weight of barium sulphate, 0.152 gm.

Weight (mgs.).	Activity.	Activity per mg,
4.075	8.95	2.20
3.375	7.51	2.22
3.85	9.05	2.35

As a mean, 1 mg. had an activity of 2.25; therefore  
152 mgs. had 342.

Activity of 1 gm. of ore is  $\frac{342}{1.713}$ , *i. e.* 200.

#### *Second Experiment.*

Weight of ore, 1.1626 gm.

Weight of barium sulphate, 0.152 gm.

Weight (mgs.).	Activity.	Activity per mg.
3.95	6.17	1.56
2.30	3.68	1.60
3.70	5.32	1.44

As a mean, 1 mg. had an activity of 1.53; therefore  
152 mgs. had 232.5.

Activity of 1 gm. of ore is  $\frac{232.5}{1.1626}$ , *i. e.* 200.

There is a small correction (about 4 per cent.) because of the presence of actinium X.

The mean activity per gram of ore is therefore 192.

§ 7. Estimation and Activity of Ionium.

The method used for separating ionium was essentially that described by Marckwald and Russell\*, which consists in adding a few milligrams of a soluble thorium salt to a solution of 1 g. of the mineral, separating the thorium quantitatively as fluoride by means of potassium fluoride, converting the fluoride into oxide by ignition, fusing the oxide with potassium hydrogen sulphate, dissolving the melt in hot water, and precipitating the thorium as hydroxide. The thorium is next freed from bodies of atomic weight 89 by one of the standard procedures. Finally the thorium is obtained in dilute sulphuric acid and then made up to 50 c.c., and aliquot parts of this solution carefully evaporated down on a copper disk on a hot plate, care being taken to get as even a film as possible.

There was fair agreement between the activities of the different disks containing the same amount of material, as the following results show :—

Weight of ore, 0.534 gs. Solution of thoria made up to 50 c.c.

5 c.c.	gave an activity of	9.61
2 c.c.	„	3.82
2 c.c.	„	3.84

Therefore as a mean 50 c.c. has an activity of 95.9, and 1 gm. of ore  $\frac{95.9}{0.534}$ , i. e. 180.

A blank test shows that the ionization due to the thorium itself was negligible. The ionization due to the radioactinium was estimated as 4 per cent. of that of ionium from the known amount of radioactinium present and the number of ions each  $\alpha$ -particle from it produces. The activity of ionium is consequently 173.

§ 8. Estimation and Activity of Proto-actinium.

6.00 gs. of the pitchblende were boiled vigorously in dilute nitric acid for an hour. The residue, after filtering, was dried and found to be active. A few milligrams of tantalum oxide were added to it and the whole fused with potassium hydroxide in a nickel crucible. The melt was dissolved in cold water, and the unattacked residue was found to be inactive. It was presumed that the whole

\* W. Marckwald and A. S. Russell, *Jahr. d. Radioakt.* vol. viii. p. 45 (1911).

of the tantalum remained in solution, together with the whole of the proto-actinium which had been in the first residue. This alkaline solution was added to the original acid filtrate, and after neutralizing with ammonia and adding a little dilute sulphuric acid the solution was boiled vigorously for fifteen minutes, on which the tantalum settled out, presumably quantitatively, in a flaky condition which was easily filtered\*. In order to free the active tantalum from radio-elements other than those of atomic number 91, it was fused with potassium hydrogen sulphate and the melt dissolved in hot water. The tantalum alone was found to be thrown out of solution. Radio-elements other than those of atomic number 91 present remained in solution. The tantalum was filtered off and the operation of fusing repeated. Finally the tantalum was ignited and weighed, the activity being measured in the form of a film in the usual way.

It follows from the chemical operations that the only active radio-element present with the tantalum after uranium  $X_2$  had decayed away was proto-actinium.

Weight of ore, 6.00 gm.

Weight of tantalum oxide, 0.011 gm.

3.0 mgs. gave an activity of 8.40

5.2 mgs.        „        „        14.28

Therefore as a mean 11 mgs. has an activity of 30.47,  
and 1 gm. of ore  $\frac{30.47}{6.00}$ , i. e. 5.08.

### § 9. Discussion of Results.

Table II. below includes the results of this research in column two. In the third column are given the numbers of ions produced per  $\alpha$ -particle when one is emitted, or per average  $\alpha$ -particle when more than one is expelled. These have been calculated from the ranges of the  $\alpha$ -particles. The fourth column contains the relative number of atoms of the different substances in equilibrium breaking up per second, and is calculated from the experimental results. The results for polonium might appear best to be used as a standard for comparison, as this element is easily separated quantitatively and its  $\alpha$ -particles are practically unabsorbed when it is in the form of a film. Ionium, however, has been chosen

\* W. G. Guy and A. S. Russell, Journ. Chem. Soc. (1923), in the press.

because its films resemble in thickness and method of preparation those of all the other substances except polonium, and it is capable of being separated quantitatively.

TABLE II.

Substance.	Activity.	No. of ions per $\alpha$ -particle $\times 10^{-3}$ .	Relative No. of atoms breaking up per second.
Pitchblende .....	1573	1.59	7.82
Uranium .....	313.5	1.22	2.04
Ionium .....	173	1.37	(1.00)
Radium.....	192	1.45	1.05
Polonium .....	200	1.58	1.00
Proto-actinium.....	5.1	1.41	.029

The table shows that

- (a) The relative activity of proto-actinium in the ore is nearly 3 per cent.
- (b) The relative activity of uranium is only about 2 per cent. greater than is to be ascribed to the expulsion of two  $\alpha$ -particles. If (a) be correct, the value in the fourth column should be 2.06.
- (c) Although the activity of radium is unexpectedly high, the results for ionium, radium, and polonium agree as well as might be expected considering the experimental difficulties and the uncertainty of the correction for relative ionization per  $\alpha$ -particle.
- (d) The value in the fourth column for pitchblende is low. Theoretically it should be 8 plus small percentages due to the ionization produced by the  $\beta$ -particles from the radio-elements in the ore, and by the  $\alpha$ -particles from the ultimate parent of the actinium series.

The results are also given in Table III. They are there compared with the calculated values of Table I. Values of the ratio proto-actinium to uranium are substituted for those of the ratio actinium series to uranium.

TABLE III.

	No branch in the Uranium series.	Branch at Uranium I.		Branch at Uranium II.		Independent isotope parent of Ac. series.		Results obtained in this research.
		3 %.	8 %.	3 %.	8 %.	3 %.	8 %.	
Whole mineral Uranium	5.23	5.31	5.47	5.24	5.26	5.25	5.29	5.00
Ionium Uranium	0.56	0.55	0.54	0.54	0.52	0.55	0.52	0.55
Radium Uranium	0.60	0.59	0.57	0.58	0.55	0.58	0.55	0.61
Polonium Uranium	0.65	0.64	0.61	0.63	0.60	0.63	0.60	0.64
Proto-actinium Uranium	.....	0.015	0.0405	0.015	0.0395	0.018	0.0435	0.016

It is seen from this table that, while there is no difficulty in deciding that the actinium series forms about 3 per cent. of the uranium series, it is not possible with the results obtained to decide whether actinium comes from a branching in the uranium series at uranium I or uranium II, or from an independent isotope. It would appear that this point can only be settled experimentally by a determination of the atomic weight of proto-actinium, and the definite proof or disproof, by Aston's method, of the existence of an isotope of uranium genetically independent of uranium I.

The results disagree with those of Boltwood in

- (a) The relative activities of polonium, ionium, and radium to uranium. His are much lower than those obtained, which are those normally to be expected.
- (b) In the ratio of uranium to one of its disintegration-products corrected for the relative ionization of these bodies, 2.04 against his 2.2.
- (c) In the ratio of the amount of the actinium series to that of the radium, 2.9 per cent. against the 8 per cent. deduced by Rutherford from his results.

On the other hand, we appear to agree with Boltwood that the ratio of the activity of the whole mineral to that of uranium is lower than is to be expected, his experimental value being 11 per cent. lower than the calculated value, ours 5 per cent. We are inclined to think that there is nothing of importance in this low result, and that it may be satisfactorily explained on two grounds:—(1) Our

assumption that there was no absorption of  $\alpha$ -particles by the material composing the films measured was possibly less true of the pitchblende films than of the others; and (2) the dimensions of our electroscope possibly prevented the long-range  $\alpha$ -particles from radium C' from ionizing to their fullest extent.

The result obtained for the activity of the actinium series referred to that of the radium series (the branching factor, if branching occurs)  $0\cdot029$ , agrees with the value of Hahn and Meitner \*,  $0\cdot03 \pm 0\cdot003$ , and is lower than Meyer's †,  $0\cdot042$ . The result is also consistent with the experimental values of the ratio of the relative activities of uranium Y and uranium X. This ratio should be equal to the above ratio if uranium Y is connected genetically with the actinium series, but it cannot be accurately interpreted owing to uncertainty concerning the relative ionization of  $\beta$ -particles of different penetrating power. Hahn ‡ found  $0\cdot021$ ; Kirsch §, at most,  $0\cdot042$ ; Guy and Russell ||  $0\cdot032$ .

#### SUMMARY.

1. The work of Boltwood on the relative activities of the radioactive constituents of a uranium mineral has been carefully repeated. Our results agree with his on the lowness of the relative activity of the mineral to that of the uranium it contains, but disagree on the relative activities of polonium, ionium, radium, and uranium. For these we find values close to those expected by theory.

2. We find the ratio of the activity of the actinium series to that of the radium series to be  $0\cdot029$ , in agreement with Hahn, but in disagreement with the value  $0\cdot08$  deduced by Rutherford from Boltwood's results, and with the value  $0\cdot04$  obtained experimentally by Meyer.

3. It is concluded that measurements along the lines of those in this paper cannot decide whether the actinium series arises as a branch of the uranium series or comes independently from an isotope of uranium.

The authors wish to thank the Government Grant Committee of the Royal Society for materials and apparatus used in this work.

Dr. Lee's Laboratory,  
Christ Church, Oxford.  
July 1923.

\* O. Hahn and L. Meitner, *Phys. Zeit.* vol. xx. p. 529 (1919).

† S. Meyer, *Wien. Anzeiger*, 133. (1920).

‡ O. Hahn, *Phys. Zeit.* vol. xiv. p. 203 (1914).

§ G. Kirsch, *Wien. Ber.* vol. cxxix. 2 a, p. 309 (1920).

|| W. G. Guy and A. S. Russell (*loc. cit.*).



XCVIII. *Partitioning of Space into Enantiomorphous Polyhedra.* By W. BARLOW, F.R.S. \*

AN Exhaustive Partitioning into Similar Plane-faced Cells of two Enantiomorphous Forms equally numerous. The cells formed have 13 faces and the unlimited system produced presents Hemihedral Cubic Symmetry.

IN 1894 the author directed attention to the partitioning of space without remainder into similar cells all of the same pattern, but presenting more than one orientation † ; and in 1914 he indicated the possibility of a partitioning into space-filling similar polyhedral cells each having 13 plane faces ‡.

A method for achieving such a partitioning will now be described.

CONSTRUCTION.

1. Draw three sets of parallel equidistant planes in three directions mutually at right angles so as to divide space into equal cubes.

2. Construct a cubic system of non-intersecting trigonal axes by drawing endless lines in the four directions of the body-diagonals of the cubes so that every cube is trans-fixed by a single diagonal only, while none of the lines thus drawn intersect ; one fourth of the total number of endless cube diagonals possible are thus drawn. But one kind of arrangement is producible by the prescribed process §.

3. Select one half of the cubes symmetrically and so that each cube of the selected set has contact at edges only with other selected cubes ; this set has face-contact with cubes belonging to the identical complementary set.

4. In each cube of a set thus selected find two points lying on the single diagonal drawn, equidistant from the cube centre and so situated that the distance apart of the two points equals the distance separating nearest points not on the same diagonal in the unlimited point-system consisting of all the points. A single individual cube of

\* Communicated by the Author. Appears also in the *Zeitschrift für Kristallographie*, Bd. lviii. pp. 605-628.

† Groth's *Zeitschr. f. Kristallogr.* xxiii. pp. 38, 59, 60. Tafel II. figs. 13, 16, 17, 18; and xxv. p. 1.

‡ Proc. Roy. Soc. London, A. vol. xci. p. 1 (1914).

§ Groth's *Zeitschr. f. Kristallogr.* xxiii. pp. 7-9.

each set is represented in figs. 1 a & 1 b. Slender wooden rods are employed to outline each skeleton cube and to supply it with a single diagonal stay which occupies the

Fig. 1 a.

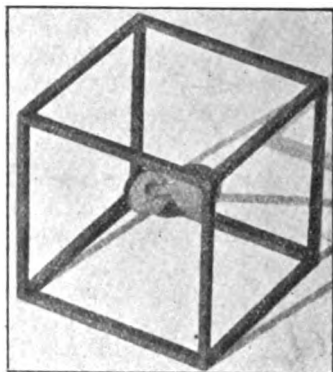


Fig. 1 b.

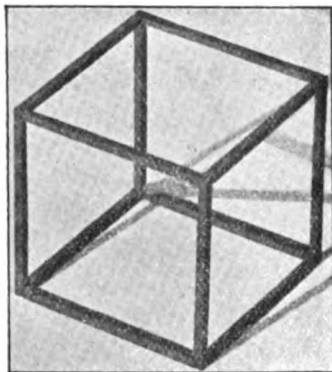
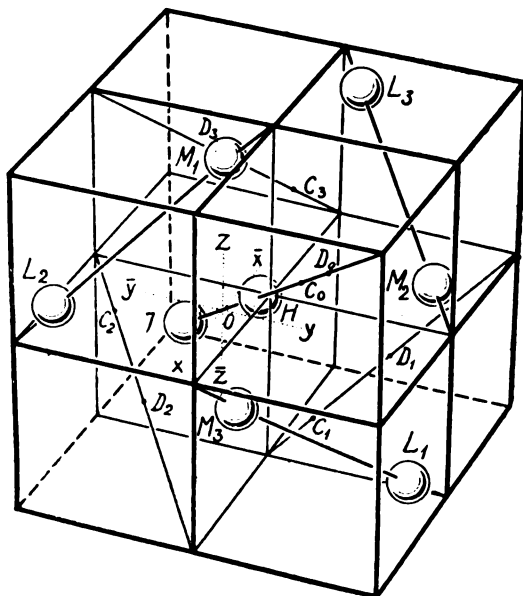


Fig. 2.



position of the diagonal selected as trigonal axis. The two points found are indicated as centres of the small spheres transfixt by this diagonal. Fig. 2 gives a compact group  
3 O 2

of 8 skeleton cubes forming a composite space-unit from which the unlimited system is developable by means of translations. The coincidence operations of the unlimited double-point-system formed of all the points are of type 1  $a_1$  in Barlow's list, centres of symmetry consisting of two kinds being present at all the centres of the cubic cells of both sets\*.

The fundamental point-system consists entirely of singular points †, and has the following properties:—

- (a) Each point lies on some trigonal axis of rotation of the unlimited system.
- (b) It is by hypothesis equidistant from the second point on this axis present in the same cell and from some other nearest points lying on other axes in other cells.
- (c) These other points are six in number, making therefore seven points equidistant from the given point. For of the 12 cubic cells with which the cell of the selected point has contact at its twelve edges, 6 are nearer to the selected point than are the remaining 6, and the former six alone furnish points equidistant with the second point in the diagonal from the selected point.
- (d) Reasoning similar to the above establishes the existence of six *next nearest* points, at slightly greater distance, equidistant from each point. These, with the seven points of (c), constitute a group of 13 points immediately surrounding every point of the point-system.

5. Next join every point with each of the 13 points thus immediately surrounding it, and through the points of bisection of these joining lines draw planes each perpendicular to its line and of such extent as to meet, but not intersect, contiguous planes thus drawn. The system of similar plane-faced cells thus produced is that required.

In consequence of the symmetry of the system the planes drawn as prescribed enclose no spaces other than these similar cells which are, as will be shown, enantiomorphous polyhedra each having 13 faces; the two enantiomorphous kinds of cell are equally numerous and similarly distributed. Fig. 3 shows a pair of the cells, one of each kind, having one face which is a regular hexagon in

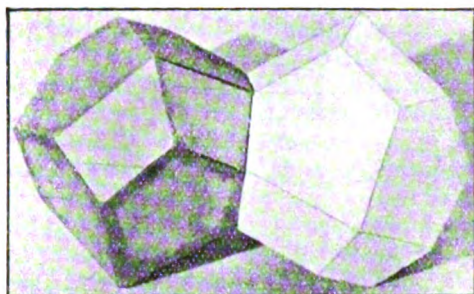
\* Groth's *Zeitschr. f. Kristallogr.* xxiii. pp. 43 & 44.

† *Ibid.* p. 60, where a general definition of a system of singular points is given.

common ; the centre of this face is a centre of symmetry. The form of cell and its properties are traced as follows\*.

As a result of the presence of the trigonal axes and of centres of symmetry which lie on these axes, an interface drawn to bisect a line joining two nearest points both on the same axis, namely through a centre of symmetry situated at the point of bisection, is, as just stated, a regular hexagon. Each angular point of this hexagon is common to two enantiomorphously-related cells separated by the hexagonal interface (see fig. 3) ; also to two other

Fig. 3.



cells, the axes of which are differently oriented and neither of them parallel to that common to the pair connected by the interface. Thus each angular point of a hexagonal interface is common to four cells.

Within each of the complementary set of skeleton cubes, which do not contain any point of the fundamental point-system, the combined operation of the centre of symmetry at the centre of this cube and the trigonal axis on which this centre lies, produces, as at the centres of symmetry just dealt with, a sixfold repetition ; but here the centre of symmetry is a point common to six of the polyhedral cells. And the trigonal axis passing through it forms the common edge of each of two triangularly-arranged sets of three cells, the three individuals of a set being in each case related by this trigonal axis, and the one set being developable from the other by an operation about the centre of symmetry just referred to.

The less regular 12 faces of a cell, which, with the

\* The arguments employed will be more readily followed with the aid of a set of skeleton cubes and a few cardboard cells constructed with the aid of the *net* given by fig. 10 below.

hexagonal face, make up the 13, fall into four groups each comprising three similar faces related by coincidence operations about the trigonal axis which passes perpendicular to the hexagonal face of the cell through its centre. The four groups display however but two distinct forms of face, the one quadrilateral the other irregular-pentagonal; but in both cases, notwithstanding identical relation to the system as a whole, two sets of three faces of each form are distinguishable on a single cell, one set bearing a different relation to this cell from that borne by the other.

A polyhedron has 19 solid angles, namely : 6 triads each consisting of three similar solid-angles equals 18, and one making the 19th through which the trigonal axis of the cell passes. The solid-angles forming a triad are, in each case, related by this trigonal axis.

As a means of locating the angular points of a polyhedron with respect to its axes and to the centre of symmetry at the middle of its hexagonal face, there are the following properties traceable on examination of the group of skeleton cubes employed :—

Each of the angular points of the polyhedron is the centre of a sphere circumscribable about a tetrahedron formed by joining some four neighbouring points of the original point-system. And in three cases the sphere passes through two more of these points, thus circumscribing an octahedron outlined by lines forming six points.

These properties are established as follows :—

Each angular point of the polyhedron is, by the construction employed, the point of intersection of at least 3 plane faces each drawn to bisect at right angles one of three lines drawn from some point of the point-system to three neighbouring points of this system. By joining the extremities of the three lines a tetrahedron is completed the centre of the circumscribing sphere of which is the point of intersection of the 3 planes.

Again, those of the cubic units which do not contain any points of the point-system are each in face-contact with six of the units containing points and are similarly related to six nearest points of this system. Consequently the centre of symmetry found in every such unit is the point of meeting of and similarly related to six polyhedra, owing to the operation of the centre of symmetry and the trigonal axis which passes through it. Further, a sphere can be circumscribed about the symmetrical octahedron produced by joining the six nearest points referred to.

The complete form and relative dimensions of a single cell are arrived at by the following steps :—

- A. Find the coordinates of any selected point of the point-system and of the 13 points of the system immediately surrounding it, as referred to axes parallel to edges of the cubic cells, the origin being at the centre of symmetry lying midway between the selected point and that nearest point of the 13 which lies on the same trigonal axis : namely, at the centre of the cubic element containing those two points. The edge of a cubic cell is taken as unit.
- B. Find the coordinates of the points of intersection of the planes drawn as prescribed to form a single polyhedral cell.
- C. Find the lengths of the various edges of a cell.
- D. Find the shapes of the plane faces of a cell.
- E. Construct a "mat" showing these faces as they would be related if, while remaining attached at single edges, they were hinged and spread out in the same plane.

#### A.

*For finding the coordinates of a selected point and the 13 points immediately surrounding it.*

The distance of each point from the centre of the cube within which it lies being the same and, by hypothesis, such that the distance apart of nearest points on the same axis is equal to that between nearest points not thus related, the value  $n$  of the distance of a point from the nearest corner of its cubic cell is readily obtainable. Thus, taking the edge of a cubic element as unity, the distance separating two nearest points on the same axis is  $\sqrt{3}-2n$ , and since two nearest points not thus related lie in a plane which is parallel to one of the three sets of cube faces, and a line drawn in this plane equidistant from the two points, parallel to a cube edge, is at a distance  $\frac{n}{\sqrt{3}}$  from each of them,

it follows that the distance apart of the two points is  $\sqrt{1+\left(\frac{2n}{\sqrt{3}}\right)^2}$ . And thus by hypothesis

$$\sqrt{3}-2n = \sqrt{1+\left(\frac{2n}{\sqrt{3}}\right)^2}$$

and

$$n = \frac{\sqrt{3}}{4}(3-\sqrt{5}) = .33082.$$

Further  $2r$ , the distance apart of nearest points,

$$= \sqrt{3} - 2n = 1.73205 - .66164 = 1.07041.$$

And the distance between next nearest points  $2s$

$$\begin{aligned} &= \sqrt{(2r)^2 + \left(1 - \frac{2n}{\sqrt{3}}\right)^2} \\ &= \sqrt{(1.07041)^2 + \left(1 - \frac{.66164}{\sqrt{3}}\right)^2} = 1.23606. \end{aligned}$$

The relative situations of the surrounding 13 points with respect to the selected point are of five kinds :

- (a) One point I lies on the trigonal axis which passes through the selected point H (comp. fig. 2).
- (b) Nearest to I and distant  $2s$  from H are three similarly situated points  $J_1, J_2, J_3$ , connected by successive rotations through  $120^\circ$  about the trigonal axis.
- (c) Next in order of distance from I and distant  $2r$  from H are three points  $K_1, K_2, K_3$ , similarly connected by the trigonal axis.
- (d) Next in order, distant  $2s$  from H, three points  $L_1, L_2, L_3$ , similarly connected.
- (e) Further from I and distant  $2r$  from H, three points  $M_1, M_2, M_3$ , similarly connected.

Since the distance of each point from the nearest corner of its cubic cell is  $n$ , and it lies on one of the trigonal axes, the value of a projection of  $n$  in each of the axes  $x, y, z$  is

$$\frac{n}{\sqrt{3}} = \frac{.33082}{1.73205} = .191 \text{ very approximately.}$$

The coordinates of each point, as referred to the angle of the cubic element in which it lies as origin, have this value ; and the coordinates of the 14 points, taking the centre of symmetry O, midway between the points H and I, as origin, and  $x, y, z$  parallel to cube edges as axes, are easily obtained and are as follows :—

	<i>x.</i>	<i>y.</i>	<i>z.</i>
For H, the point selected as centre of the polyhedral cell. $x=\frac{1}{2}-\cdot191$ =	+ ·309	+ ·309	+ ·309
I	- ·309	- ·309	- ·309
Nearest triad to I .....	$\left\{ \begin{array}{l} J_1 \\ J_2 \\ J_3 \end{array} \right.$	$\left\{ \begin{array}{l} - \cdot691 \\ - \cdot309 \\ + \cdot691 \end{array} \right.$	$\left\{ \begin{array}{l} - \cdot309 \\ + \cdot691 \\ - \cdot691 \end{array} \right.$
Next nearest triad to I .....	$\left\{ \begin{array}{l} K_1 \\ K_2 \\ K_3 \end{array} \right.$	$\left\{ \begin{array}{l} + \cdot691 \\ + \cdot309 \\ - \cdot691 \end{array} \right.$	$\left\{ \begin{array}{l} + \cdot309 \\ - \cdot691 \\ + \cdot691 \end{array} \right.$
For next triad .....	$\left\{ \begin{array}{l} L_1 \\ L_2 \\ L_3 \end{array} \right.$	$\left\{ \begin{array}{l} + \cdot691 \\ +1\cdot309 \\ - \cdot309 \end{array} \right.$	$\left\{ \begin{array}{l} +1\cdot309 \\ - \cdot309 \\ + \cdot691 \end{array} \right.$
Further from I... ..	$\left\{ \begin{array}{l} M_1 \\ M_2 \\ M_3 \end{array} \right.$	$\left\{ \begin{array}{l} + \cdot691 \\ + \cdot309 \\ +1\cdot309 \end{array} \right.$	$\left\{ \begin{array}{l} + \cdot309 \\ +1\cdot309 \\ + \cdot691 \end{array} \right.$

### B.

*For finding the coordinates of the points of intersection of the planes drawn as prescribed to form a single polyhedral cell.*

These points are, as already stated, 19 in number and are at the centre of spheres circumscribing irregular tetrahedra outlined by joining appropriate sets of four of the points just located. Three of these spheres, however, pass through more than four of the points; they circumscribe octahedra, each of which is outlined by joining six of these points, appropriately chosen, each octahedron possessing a single trigonal axis.

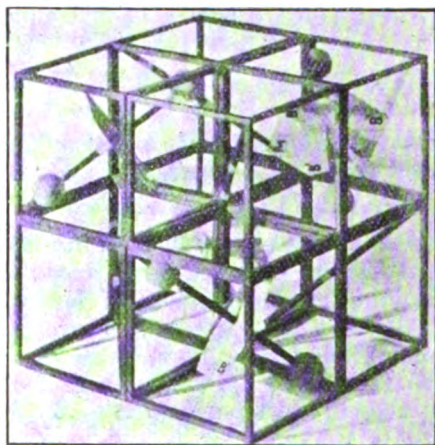
Now, as already pointed out, the existence of a centre of symmetry at the centre of each cubic element and of a single trigonal axis of rotation passing through this centre involves a sixfold regular hexagonal repetition of any point not a singular-point, which is present in the plane that passes through the centre of symmetry at right angles to the axis.

Let the 6 points of meeting of the plane bisecting the line HI at right angles with other pairs of the bisecting planes, which 6 points thus form the angular points of a regular hexagon, be lettered A', A'', A''', B', B'', B''' ; the three A's and also the three B's are related by the trigonal axis, while the B's are derivable from the A's by an operation about the centre of symmetry referred to situated at the centre of the cubic cell. The hexagonal interface thus



defined separates and is a common face of two enantiomorphous cells having the mirror image relation consequent on the presence of the centre of symmetry. Such interfaces are found in one only of the two systems of edge-contact cubic cells which together constitute the entire system of these cells filling space: namely, in the set containing the points of the fundamental point-system; they each indicate the only six points of intersection found in the cell containing it. Plane hexagons of appropriate size, cut out of cardboard, can be fixed, one in each of the cells in which these points are present, so as to show the

Fig. 4.



situations of a number of the points of intersection (fig. 4). Details enabling this to be done will be given immediately.

Other points of intersection of the planes, all of which are singular points above referred to, are found in the complementary set of cubic elements which do not contain any points of the fundamental point-system. These other points of intersection are situated three on each of the portion of a trigonal axis contained within each of the cubic elements of this complementary set. The central point of the three is at the centre of symmetry of the containing cubic cell; the other two points of a trio are equidistant from this centre of symmetry in positions determined later.

(a) As to the relative situations of the hexagonally-arranged group of 6 points of intersection present in the cubic cell with centre O :

The centre of the sphere circumscribing the tetrahedron outlined by lines joining points...

	H, I, J <sub>1</sub> , K <sub>2</sub>	is lettered	A
"	H, I, J <sub>2</sub> , K <sub>3</sub>	"	A''
"	H, I, J <sub>3</sub> , K <sub>1</sub>	"	A'''
"	I, H, K <sub>1</sub> , J <sub>2</sub>	"	B'
"	I, H, K <sub>2</sub> , J <sub>3</sub>	"	B''
"	I, H, K <sub>3</sub> , J <sub>1</sub>	"	B'''

The relative situations and orientations of some of the other hexagonal plane groups of points of intersection found, one group in each of the cubic cells of the half-system of these cells containing points of the fundamental point-system, will now be considered.

The cubic cell containing the origin O, which point is the centre of the complex consisting of the pair of enantiomorphous cells having the hexagonal interface A', A'', A''', B', B'', B''' in common, is surrounded by 12 cubic cells in edge-contact with this central cell and occupied in the same manner. Each of these cubic cells bears the same relation as the central cell does to the unlimited system. These 12 cells are all equidistant from the origin O ; they form six pairs, each consisting of two cells so related that one is developable from the other by operating the centre of symmetry at O. Otherwise considered they may be regarded as forming four sets, the individuals of each set of three being related by the trigonal axis passing through O. As to two of these sets, each of the three cells forming the set is so constituted and related that a corner of each and a corner of the central cell all four coincide on the trigonal axis passing through O. And as to the remaining two sets, the centres of all six cells lie hexagonally arranged in the plane which cuts the trigonal axis at right angles in the point O. The respective orientations of the 12 cubic cells referred to and the situation of their contents are conveniently arrived at by operating appropriate digonal screw coincidence movements which locate the 12 centres of the cells and their respective trigonal axes with reference to the position and orientation of the central cubic cell and its contents. This work can, however, be curtailed somewhat by resorting to the use of the centre of symmetry O. A general statement of the process employed for locating a hexagonal group in each of the 12 cubic cells, accompanied

by precise dimensions, is given in tabular form later (p. 944). In each case the appropriate digonal screw movement about an axis, having one of the three directions of the edges of the cubic cells, is resolved into a rotation of  $180^\circ$  about an axis in the same direction, which passes through the origin O, followed by two translations of  $+1$  or  $-1$ , as the case may be, in two of the three axial directions, such being chosen as to direction and value as are found to furnish appropriate components.

(b) As to those points of intersection of the planes which are *singular-points* lying on trigonal axes within the complementary sets of cubic elements which do not contain points of the fundamental point-system :

The centre of the sphere circumscribing the tetrahedron outlined by joining the 4 points	H, M <sub>1</sub> , M <sub>2</sub> , M <sub>3</sub> is lettered	C <sub>0</sub>
" " "	K <sub>1</sub> , J <sub>2</sub> , L <sub>1</sub> , H " "	C <sub>1</sub>
" " "	K <sub>2</sub> , L <sub>2</sub> , J <sub>3</sub> , H " "	C <sub>2</sub>
" " "	K <sub>3</sub> , J <sub>1</sub> , L <sub>3</sub> , H " "	C <sub>3</sub>
The centre of the skeleton cube containing the point C <sub>0</sub> is equidistant from 6 points of the fundamental point-system and is the centre of the sphere circumscribing the octahedron located by these points; it is lettered .....		
That containing the point .....		D <sub>0</sub>
" " " .....	C <sub>1</sub> is lettered	D <sub>1</sub>
" " " .....	C <sub>2</sub> " "	D <sub>2</sub>
" " " .....	C <sub>3</sub> " "	D <sub>3</sub>

The coordinates of the points of intersection of the various planes drawn as indicated are ascertained in the following manner :—

As to A'.

Three of the planes passing through this point respectively bisect at right angles three lines joining nearest points of the point-system, viz. HK<sub>2</sub>, IJ<sub>1</sub>, and J<sub>1</sub>K<sub>2</sub>. And since these three lines are parallel to the planes *yz*, *xz*, and *xy* respectively, the three planes are respectively parallel to axis *x*, axis *y*, and axis *z*.

Draw three planes through the origin O parallel to these three planes. As a consequence of this parallelism :

In the case of the first plane the ratio  $\frac{y}{x}$ , in that of the second  $\frac{x}{z}$ , in the case of the third  $\frac{x}{y}$  is constant for every point in the parallel plane.

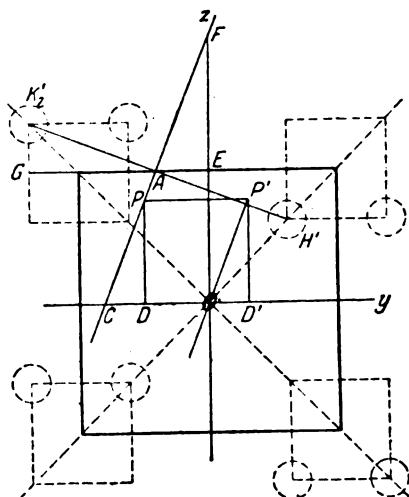
The other points of intersection possess a similar property, and as a consequence the work of ascertaining the coordinates

of all the points of intersection is comparatively simple. The following is the process in detail in the case of  $A'$ .

In fig. 5,  $H'K'_2$  is the projection of the line  $HK_2$  on plane  $yz$  to which plane this line is parallel, and  $CAF$  is the trace of the plane perpendicular to the line through its middle point. Through the origin  $O$  draw  $OP'$  parallel to  $CAF$  and  $PP'$  parallel to axis  $y$  through any point  $P$  in the trace  $CAF$ , the coordinates of this point being  $x, y, z$ .

Also  $PD$  and  $P'D'$  parallel to axis  $z$ .

Fig. 5.



Then

$$\begin{aligned} \frac{D'O}{D'P'} &= \tan OP'D' = \tan CPD = \tan AFE \\ &= \tan K'_2AG = \frac{\cdot 191}{\frac{1}{2}} = \cdot 382. \end{aligned}$$

But  $\frac{D'O}{D'P'}$  also  $= \frac{CD}{DP'} \cdot \frac{OC - OD}{z} = \frac{OC + y}{z} = \cdot 382.$

Again,

$$\frac{AE}{EF} = \tan AFE = \cdot 382$$

and  $AE = EG - AG = (\cdot 5 + \cdot 191) - \cdot 5 = \cdot 191;$

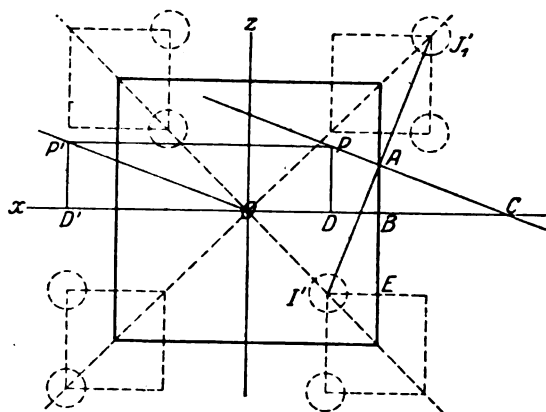
$$\therefore EF = \frac{AE}{\tan AFE} = \frac{\cdot 191}{\cdot 382} = \cdot 5 = EO = \frac{OF}{2}$$

and  $OC = 2AE = \cdot 382;$

$$\therefore \frac{OC + y}{z} = \frac{\cdot 382 + y}{z} = \cdot 382 \text{ and } y = -\cdot 382(1 - z). \quad (1)$$

Again, fig. 6 gives the projection  $I'J'_1$  of the line  $IJ_1$  on plane  $xz$  and the trace  $CAP$  of the plane perpendicular to this line through its middle point.

Fig. 6.



Through the origin  $O$  draw  $OP'$  parallel to this trace and  $PP'$  parallel to axis  $x$  through any point  $P$  in this trace, the coordinates of this point being  $-x$  and  $z$ ; also  $P'D'$  parallel to axis  $z$ .

Then

$$\frac{D'O}{D'P'} = \tan OP'D' = \tan CPD = \tan AI'E = \frac{\frac{1}{2}}{\cdot 191} = \frac{1}{\cdot 382};$$

and

$$\frac{D'O}{D'P'} = \frac{DC}{D\bar{P}} = (\text{since } x = -OD) \frac{OC + x}{z}.$$

Now

$$\frac{AB}{BC} = \tan ACB = \tan I'AE = \frac{\cdot 191}{\cdot 5} = \cdot 382$$

and

$$AB = AE - BE = \cdot 5 - (\cdot 5 - \cdot 191) = \cdot 191,$$

$$\therefore BC = \cdot 5.$$

And since

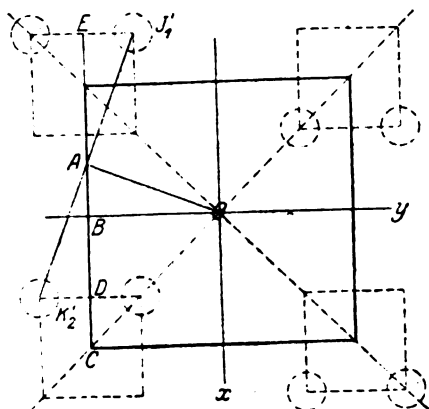
$$OB = \cdot 5, \quad OC = 1, \quad \text{and} \quad PP' = DD' = 1,$$

$$\therefore \frac{OC + x}{z} = \frac{1 + x}{z} = \frac{D'O}{D'P'} = \tan AI'E = \frac{1}{\cdot 382}$$

$$\text{and} \quad z = \cdot 382(1 + x). \quad \dots \dots \dots (2)$$

Again, fig. 7 gives the projection  $J_1'K_2'$  on plane  $xy$  and the trace AO of the plane perpendicular to this line through its middle point.

**Fig. 7.**



Since

$$\angle BAO = \angle DK_2'A \quad \text{and} \quad BO = \frac{DE}{2} = AD,$$

and therefore

$$AB = DK_3',$$

the trace  $AO$  passes through  $O$ , and for every point in this line

$$\frac{-x}{-y} = \frac{DK_2'}{AD} = \frac{.191}{.5};$$

$$\therefore x = .382 \cdot y. \quad \cdot \cdot \cdot \cdot \cdot (3)$$

For the point of intersection  $A'$  of the three planes all three equations (1) (2) and (3) hold good. And from (1) and (3)

$$\frac{x}{.382} = -.382(1-z).$$

Therefore substituting the value of  $z$  obtained from (2),

$$\frac{x}{.382} = -.382\{1 - .382(1 + x)\}.$$

# 944 *Partitioning of Space into Enantiomorphous Polyhedra.*

TABLE giving method of derivation of the relative situations and orientations, and also the respective coordinates of the constituent points, of 12 next surrounding hexagonal groups of points of intersection from the situation and orientation of the group found in the central cell containing the origin O, which group as above ascertained consists of the 6 points:—

- (1) A', the coordinates of which are  $x = -0.955$ ,  $y = -0.25$ ,  $z = +0.3455$ .
- (2) A'', " " "  $-0.25$ ,  $+0.3455$ ,  $-0.955$ .
- (3) A''', " " "  $+0.3455$ ,  $-0.955$ ,  $-0.25$ .
- (4) B', " " "  $+0.955$ ,  $+0.25$ ,  $-0.3455$ .
- (5) B'', " " "  $+0.25$ ,  $-0.3455$ ,  $+0.955$ .
- (6) B''', " " "  $-0.3455$ ,  $+0.955$ ,  $+0.25$ .

Designation of point the coordinates of which are required.	Derived from point designated.	Result of application of component rotation of 180° about axis of the appropriate screw spiral movement.									The required coordinates developed by the screw movement.		
		Axial direction.	Derived coordinates after rotation only.			Component translations added.							
									x.	y.	z.	x.	y.
A <sub>1</sub> '	A'	x	-0.955	+0.25	-0.3455	+1	0	+1	+0.045	+0.25	+0.645		
A <sub>1</sub> ''	A''	"	-0.25	-0.3455	+0.955	+1	0	+1	+0.75	-0.3455	+1.0955		
A <sub>1</sub> '''	A'''	"	+0.3455	+0.955	+0.25	+1	0	+1	+1.3455	+0.955	+1.25		
B <sub>1</sub> '	B'	"	+0.955	-0.25	+0.3455	+1	0	+1	+1.0955	-0.25	+1.3455		
B <sub>1</sub> ''	B''	"	+0.25	+0.3455	-0.955	+1	0	+1	+1.25	+0.3455	+0.045		
B <sub>1</sub> '''	B'''	"	-0.3455	-0.955	-0.25	+1	0	+1	+0.645	-0.955	+0.75		
A <sub>2</sub> '	A'	y	+0.955	-0.25	-0.3455	+1	+1	0	+1.0955	+0.75	-0.3455		
A <sub>2</sub> ''	A''	"	+0.25	+0.3455	+0.955	+1	+1	0	+1.25	+1.3455	+0.045		
A <sub>2</sub> '''	A'''	"	-0.3455	-0.955	+0.25	+1	+1	0	+0.645	+0.045	+0.25		
B <sub>2</sub> '	B'	"	-0.955	+0.25	+0.3455	+1	+1	0	+0.045	+1.25	+0.3455		
B <sub>2</sub> ''	B''	"	-0.25	-0.3455	-0.955	+1	+1	0	+0.75	+0.645	-0.955		
B <sub>2</sub> '''	B'''	"	+0.3455	+0.955	-0.25	+1	+1	0	+1.3455	+1.0955	-0.25		
A <sub>3</sub> '	A'	z	+0.955	+0.25	+0.3455	0	+1	+1	+0.955	+1.25	+1.3455		
A <sub>3</sub> ''	A''	"	+0.25	-0.3455	-0.955	0	+1	+1	+0.25	+0.645	+0.045		
A <sub>3</sub> '''	A'''	"	-0.3455	+0.955	-0.25	0	+1	+1	-0.3455	+1.0955	+0.75		
B <sub>3</sub> '	B'	"	-0.955	-0.25	-0.3455	0	+1	+1	-0.955	+0.75	+0.645		
B <sub>3</sub> ''	B''	"	-0.25	+0.3455	+0.955	0	+1	+1	-0.25	+1.3455	+1.0955		
B <sub>3</sub> '''	B'''	"	+0.3455	-0.955	+0.25	0	+1	+1	+0.3455	+0.045	+1.25		
A <sub>4</sub> '	A'	x	-0.955	+0.25	-0.3455	-1	0	-1	-1.0955	+0.25	-1.3455		
A <sub>4</sub> ''	A''	"	-0.25	-0.3455	+0.955	-1	0	-1	-1.25	-0.3455	-0.045		
A <sub>4</sub> '''	A'''	"	+0.3455	+0.955	+0.25	-1	0	-1	-0.645	+0.955	-0.75		
B <sub>4</sub> '	B'	"	+0.955	-0.25	+0.3455	-1	0	-1	-0.045	-0.25	-0.645		
B <sub>4</sub> ''	B''	"	+0.25	+0.3455	-0.955	-1	0	-1	-0.75	+0.3455	-1.0955		
B <sub>4</sub> '''	B'''	"	-0.3455	-0.955	-0.25	-1	0	-1	-1.3455	-0.955	-1.25		

Designation of point the coordinates of which are required.	Derived from point designated.	Result of application of component rotation of 180° about axis of the appropriate screw spiral movement.						The required coordinates developed by the screw movement.			
		Axial direction.	Derived coordinates after rotation only.			Component translations added.					
			<i>x.</i>	<i>y.</i>	<i>z.</i>	<i>x.</i>	<i>y.</i>	<i>z.</i>	<i>x.</i>	<i>y.</i>	<i>z.</i>
A <sub>5</sub> '	A'	<i>y</i>	+0955	-25	-3455	-1	-1	0	-9045	-125	-3455
A <sub>5</sub> ''	A''	"	+25	+3455	+0955	-1	-1	0	-75	-6545	+0955
A <sub>5</sub> '''	A'''	"	-3455	-0955	+25	-1	-1	0	-13455	-10955	+25
B <sub>5</sub> '	B'	"	-0955	+25	+3455	-1	-1	0	-10955	-75	+3455
B <sub>5</sub> ''	B''	"	-25	-3455	-0955	-1	-1	0	-125	-13455	-0955
B <sub>5</sub> '''	B'''	"	+3455	+0955	-25	-1	-1	0	-6545	-9045	-25
A <sub>6</sub> '	A'	<i>z</i>	+0955	+25	+3455	0	-1	-1	+0955	-75	-6545
A <sub>6</sub> ''	A''	"	+25	-3455	-0955	0	-1	-1	+25	-13455	-10955
A <sub>6</sub> '''	A'''	"	-3455	+0955	-25	0	-1	-1	-3455	-9045	-125
B <sub>6</sub> '	B'	"	-0955	-25	-3455	0	-1	-1	-0955	-125	-13455
B <sub>6</sub> ''	B''	"	-25	+3455	+0955	0	-1	-1	-25	-6545	-9045
B <sub>6</sub> '''	B'''	"	+3455	-0955	+25	0	-1	-1	+3455	-10955	-75
A <sub>7</sub> '	A'	<i>x</i>	-0955	+25	-3455	+1	0	-1	+9045	+25	-13455
A <sub>7</sub> ''	A''	"	-25	-3455	+0955	+1	0	-1	+75	-3545	-9045
A <sub>7</sub> '''	A'''	"	+3455	+0955	+25	+1	0	-1	+13455	+0955	-75
B <sub>7</sub> '	B'	"	+0955	-25	+3455	+1	0	-1	+10955	-25	-6545
B <sub>7</sub> ''	B''	"	+25	+3455	-0955	+1	0	-1	+125	+3455	-10955
B <sub>7</sub> '''	B'''	"	-3455	-0955	-25	+1	0	-1	+6545	-0955	-125
A <sub>8</sub> '	A'	<i>y</i>	+0955	-25	-3455	-1	+1	0	-9045	+75	-3455
A <sub>8</sub> ''	A''	"	+25	+3455	+0955	-1	+1	0	-75	+13455	+0955
A <sub>8</sub> '''	A'''	"	-3455	-0955	+25	-1	+1	0	-13455	+9045	+25
B <sub>8</sub> '	B'	"	-0955	+25	+3455	-1	+1	0	-10955	+125	+3455
B <sub>8</sub> ''	B''	"	-25	-3455	-0955	-1	+1	0	-125	+6545	-0955
B <sub>8</sub> '''	B'''	"	+3455	+0955	-25	-1	+1	0	-6545	+10955	-25
A <sub>9</sub> '	A'	<i>z</i>	+0955	+25	+3455	0	-1	+1	+0955	-75	+13455
A <sub>9</sub> ''	A''	"	+25	-3455	-0955	0	-1	+1	+25	-13455	+9045
A <sub>9</sub> '''	A'''	"	-3455	+0955	-25	0	-1	+1	-3455	-9045	+75
B <sub>9</sub> '	B'	"	-0955	-25	-3455	0	-1	+1	-0955	-125	+6545
B <sub>9</sub> ''	B''	"	-25	+3455	+0955	0	-1	+1	-25	-6545	+10955
B <sub>9</sub> '''	B'''	"	+3455	-0955	+25	0	-1	+1	+3455	-10955	+125
A <sub>10</sub> '	A'	<i>x</i>	-0955	+25	-3455	-1	0	+1	-10955	+25	+6545
A <sub>10</sub> ''	A''	"	-25	-3455	+0955	-1	0	+1	-125	-3435	+10955
A <sub>10</sub> '''	A'''	"	+3455	+0955	+25	-1	0	+1	-6545	+0955	+125
B <sub>10</sub> '	B'	"	+0955	-25	+3455	-1	0	+1	-9045	-25	+13455
B <sub>10</sub> ''	B''	"	+25	+3455	-0955	-1	0	+1	-75	+3455	+9045
B <sub>10</sub> '''	B'''	"	-3455	-0955	-25	-1	0	+1	-13455	-0955	+75
A <sub>11</sub> '	A'	<i>y</i>	+0955	-25	-3455	+1	-1	0	+10955	-125	-3455
A <sub>11</sub> ''	A''	"	+25	+3455	+0955	+1	-1	0	+125	-6545	+0955
A <sub>11</sub> '''	A'''	"	-3455	-0955	+25	+1	-1	0	+6545	-10955	+25
B <sub>11</sub> '	B'	"	-0955	+25	+3455	+1	-1	0	+9045	-75	+3455
B <sub>11</sub> ''	B''	"	-25	-3455	-0955	+1	-1	0	+75	-13455	-0955
B <sub>11</sub> '''	B'''	"	+3455	+0955	-25	+1	-1	0	+13455	-9045	-25
A <sub>12</sub> '	A'	<i>z</i>	+0955	+25	+3455	0	+1	-1	+0955	+125	-6545
A <sub>12</sub> ''	A''	"	+25	-3455	-0955	0	+1	-1	+25	+6545	-10955
A <sub>12</sub> '''	A'''	"	-3455	+0955	-25	0	+1	-1	-3455	+10955	-125
B <sub>12</sub> '	B'	"	-0955	-25	-3455	0	+1	-1	-0955	+75	-13455
B <sub>12</sub> ''	B''	"	-25	+3455	+0955	0	+1	-1	-25	+13455	-9045
B <sub>12</sub> '''	B'''	"	+3455	-0955	+25	0	+1	-1	+3455	+9045	-75



Thus

$$x\{1-(\cdot382)^3\} = (\cdot382)^3 - (\cdot382)^2.$$

Now

$$1 - (\cdot382)^3 = \cdot944257$$

$$\text{and } (\cdot382)^3 - (\cdot382)^2 = -\cdot09018.$$

Therefore the coordinates of A' are very approximately

$$x = -\frac{\cdot09018}{\cdot944257} = -\cdot0955,$$

$$y = \frac{x}{\cdot382} = \frac{\cdot0955}{\cdot382} = -\cdot25,$$

$$z = \cdot382(1+x) = \cdot382 \times \cdot9045 = \cdot3455.$$

The coordinates of the remaining five points of intersection of the same group, A'', A''', B', B'', B''', are deduced from those of A' ( $x = -\cdot0955$ ,  $y = -\cdot25$ ,  $z = \cdot3455$ ) as follows :

A rotation with clock-hands of  $120^\circ$  about the trigonal axis of  $120^\circ$  which transfers axis  $y$  to the position of axis  $x$  carries A' to the position of A'', and a second such rotation locates the position of A'''. Therefore writing  $z$  for  $x$ ,  $x$  for  $y$ , and  $y$  for  $z$ , we deduce from the coordinates of A' just stated,

those of A'' :  $x = -\cdot25$ ,  $y = +\cdot3455$ ,  $z = -\cdot0955$  ;  
and those of A''' :  $x = +\cdot3455$ ,  $y = -\cdot0955$ ,  $z = -\cdot25$ .

Further, by operating the centre of symmetry at O we derive from the coordinates of A' those of B' :

$$x = +\cdot0955, \quad y = +\cdot25, \quad z = -\cdot3455 ;$$

from those of A'' the coordinates of B'' :

$$x = +\cdot25, \quad y = -\cdot3455, \quad z = +\cdot0955 ;$$

and from those of A''', the coordinates of B''' :

$$x = -\cdot3455, \quad y = +\cdot0955, \quad z = +\cdot25.$$

The coordinates of the six points of each of the 12 hexagonal groups, found respectively in the 12 cubic cells having edge-contact with the central cell, are obtained as in the Table from those just recorded by means of the appropriate screw-movements above referred to (p. 939), the results being in some cases facilitated by operating with the centre of symmetry O.

Besides the above there are, as already intimated, present in the complex consisting of 8 cubic elements two other types of points of intersection of the planes, both of which lie on trigonal axes and are consequently singular points. Those four which are marked  $C_0, C_1, C_2, C_3$  are, as in the previous cases, tetrahedron centres, the four solid angles of the tetrahedra being points of the fundamental point-system. The remaining points of intersection, four of which are marked  $D_0, D_1, D_2, D_3$  in the model, lie at the centres of spheres circumscribing octahedra outlined by joining nearest points in certain octahedral complexes consisting of six points of the point-system. These points of intersection are found at the centres of the half of the cubic elements not containing any points of the fundamental point-system. The required coordinates are derived as follows:—

As to  $C_0$ .

The coordinates of this point, which is the centre of the sphere circumscribing the tetrahedron  $H, M_1, M_2, M_3$  are ascertained as follows:—

The tetrahedron is very symmetrical, three of its edges forming an equilateral triangle  $M_1, M_2, M_3$ , and the

Fig. 8 a.

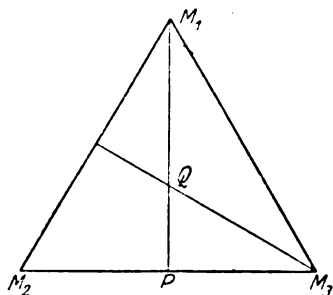
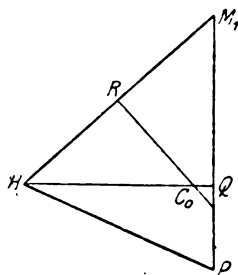


Fig. 8 b.



angular point  $H$  being equidistant from  $M_1, M_2, M_3$ . Fig. 8 a represents the equilateral base, fig. 8 b a section through  $M_1QP$  containing the trigonal axis  $HC_0Q$  about which  $M_1, M_2, M_3$  are symmetrically disposed.

$$M_1M_2 = M_2M_3 = M_3M_1 = 2s \quad (\text{see p. 936})$$

$$\text{and } HM_1 = HM_2 = HM_3 = 2r \quad (\text{see p. 936}).$$

3 P 2

The coordinates of  $C_0$  are

$$x = y = z = \frac{OC_0}{\sqrt{3}}.$$

Now

$$OC_0 = OH + HC_0 \quad \text{and} \quad OH = r,$$

while (fig. 8 *b*)

$$HC_0 = \frac{HR}{\cos C_0HR} = \frac{r}{\cos QHM_1};$$

but (see fig. 8 *a*)

$$\begin{aligned} \sin QHM_1 &= \frac{M_1Q}{HM_1} = \frac{\frac{s}{\cos 30^\circ}}{2r} = \frac{2s}{2r\sqrt{3}} \\ &= \frac{1.23606}{1.07041 \times 1.73205} = .667, \end{aligned}$$

and consequently

$$\angle QHM_1 \text{ or } C_0HM_1 = 41^\circ 50'.$$

Therefore

$$\begin{aligned} OC_0 &= r + \frac{r}{\cos C_0HM_1} = r \left( 1 + \frac{1}{\cos 41^\circ 50'} \right) \\ &= r \left( 1 + \frac{1}{.7450881} \right) = (.535205) \left( \frac{1.7450881}{.7450881} \right) = 1.2535. \end{aligned}$$

And the coordinates of  $C_0$  are

$$+.72371; \quad +.72371; \quad +.72371.$$

As to  $C_1, C_2, C_3$ .

The coordinates of  $C_0$  are as above derived :

$$x = y = z = .72371 = .5 + .22371.$$

On examination of the models represented by figs. 2, 3, and 10, it is found that

$$\begin{aligned} \text{The coordinates of } C_1 \text{ are } x &= .5 - .22371 = .27629 \\ y &= .5 + .22371 = .72371 \\ z &= -(.5 - .22371) = -.27629. \\ \text{,, ,, } C_2 \text{ are } x &= .5 + .22371 = .72371 \\ y &= -(.5 - .22371) = -.27629 \\ z &= .5 - .22371 = .27629. \\ \text{,, ,, } C_3 \text{ are } x &= -(.5 - .22371) = -.27629 \\ y &= .5 - .22371 = .27629 \\ z &= .5 + .22371 = .72371. \end{aligned}$$

Finally as to the coordinates of the centre points of the cubic cells not containing any points of the fundamental point-system.

The coordinates of  $D_0$ :  $x = y = z = 1$ ;

„ „  $D_1$ :  $x = 0, y = 1, z = 0$ ;

„ „  $D_2$ :  $x = 1, y = 0, z = 0$ ;

„ „  $D_3$ :  $x = 0, y = 0, z = 1$ .

### C.

*To find the lengths of the various edges of the polyhedral cells formed.*

These edges, which in a single cell are 30 in number, are in their relations to the system as a whole of four kinds only:

- a. Those which form sides of the hexagonal faces. These faces, it will be remembered, are found in those of the skeleton cubes which contain points of the fundamental point-system. Nine such sides or edges are found on each polyhedral cell; six of them form sides of its hexagonal face and the remaining three are sides of hexagonal faces of the adjoining cells.
- b. Those which connect a point of the kind C situated on a trigonal axis with the nearest corner of a hexagonal face. Nine of these edges are found in each cell. Three of them meet on its axis as at point  $C_0$ ; three others connect three angular points of its hexagonal face with other points of the kind C; the remaining three connect points of the hexagonal faces in adjoining cells with points of the kind C.
- c. Those which coincide with some trigonal axis connecting a point of kind C with a corresponding point of kind D. Of these edges there are three in each cell.
- d. Those which connect each angular point of a hexagonal interface with the nearest centre of kind D. Of these edges there are nine in each cell; three of them have respectively an extremity at three alternate angles of the hexagonal face of the selected cell; and the remaining six are connected with angles of hexagonal faces of neighbouring cells.

As to the length of those of kind *a* :—

Since the side of a hexagonal face equals the line joining its centre with one of its angular points, its length is

$$\sqrt{x^2 + y^2 + z^2} \text{ (as stated for the point of intersection } A') \\ = \sqrt{(-.0955)^2 + (-.25)^2 + (.3455)^2} = \sqrt{.191} = .43702.$$

As to that of kind *b* :—

For finding the edge which connects an angle of a hexagonal face with a nearest point of the kind *C*, *e. g.*,  $A_1'$  with  $C_0$  :

$$\begin{array}{lll} \text{The coordinates of } A_1' \text{ are } & \overset{x.}{+.9045}, & \overset{y.}{+}.25, & \overset{z.}{+}.6545, \\ & \text{and those of } C_0 \text{ are } & \overset{x.}{+.72371}, & \overset{y.}{+}.72371, & \overset{z.}{+}.72371. \end{array}$$

Thus edge  $A_1'C_0$

$$\begin{aligned} &= \sqrt{(.9045 - .72371)^2 + (.25 - .72371)^2 + (.6545 - .72371)^2} \\ &= \sqrt{(.18079)^2 + (.47371)^2 + (.06921)^2} \\ &= \sqrt{.032685 + .224401 + .00479} = \sqrt{.261476} = .51135. \end{aligned}$$

Another such edge  $B''C_3$  calculated in the same manner gives an identical result.

As to that of kind *c* :—

For finding the edge which coincides with a trigonal axis ; for example, that which connects  $C_0$  with  $D_0$ , the centre of the skeleton cube containing  $C_0$  and  $D_0$  :

$$\begin{array}{lll} \text{The coordinates of } C_0 \text{ are } & \overset{x.}{+.72371}, & \overset{y.}{+}.72371, & \overset{z.}{+}.72371, \\ & \text{and those of } D_0 \text{ are } & \overset{x.}{+}1, & \overset{y.}{+}1, & \overset{z.}{+}1. \end{array}$$

Thus edge  $C_0D_0$ , which lies outside the cell figured,

$$\begin{aligned} &= \sqrt{(1 - .72371)^2 + (1 - .72371)^2 + (1 - .72371)^2} \\ &= \sqrt{3(.27629)^2} = .47855. \end{aligned}$$

The edges of kind *c* of the cell represented in fig. 10 are  $C_1D_1$ ,  $C_2D_2$ ,  $C_3D_3$  ; they furnish results identical with that just obtained for  $C_0D_0$ .

As to that of kind *d* :—

For finding the edge which connects an angle of a

hexagonal face with the nearest cube centre of the kind D ; for example, the line A'D<sub>3</sub> :

The coordinates of A' are  $-\cdot0955^x, -\cdot25^y, +\cdot3455^z$ ,  
and those of D<sub>3</sub> are 0, 0, 1.

Thus edge A'D<sub>3</sub>

$$= \sqrt{(\cdot0955)^2 + (\cdot25)^2 + (1 - \cdot3455)^2}$$

$$= \sqrt{\cdot00912 + \cdot06250 + \cdot42837} = \sqrt{\cdot5} = \cdot707107.$$

The edges of kind *d* of the cell represented are A'D<sub>3</sub>, A''D<sub>1</sub>, A'''D<sub>2</sub>.

#### D.

*To find the shapes of the polygonal faces of a cell other than the hexagonal face.*

This is accomplished by dividing these faces into triangles. The sides of the triangles which are not edges are diagonals of the polygons ; their lengths are ascertained in the same manner as those of the cell-edges.

There are seven sets of these lines, examples of each set being

A'C<sub>3</sub>, B'''D<sub>3</sub>, A'B<sub>1</sub>'', A<sub>1</sub>C<sub>2</sub>, C<sub>2</sub>D<sub>3</sub>, B''D<sub>3</sub>, B''B<sub>1</sub>''

respectively (fig. 9).

Fig. 9 a.

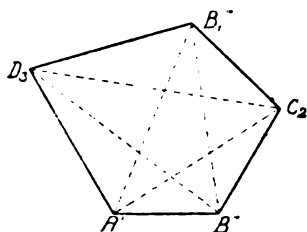
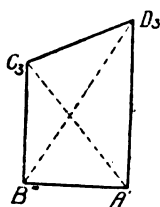


Fig. 9 b.



Three of these in conjunction with the lengths of the edges suffice for ascertaining the shapes of the irregular faces ; but it has to be borne in mind that a face of an ascertained shape and position bears a different relation to the two enantiomorphous forms of cell between which it is found.

As already intimated, there are but three kinds of inter-faces : a hexagonal, a quadrilateral, and a five-sided.

All seven sets of face diagonals are here ascertained for the purpose of checking the accuracy of the calculations.

For finding  $A'C_3$  :

The coordinates of  $A'$  are  $-.0955, -.2500, .3455$  ;  
those of  $C_3$  are  $-.27629, +.27629, .72371$ .

Thus  $A'C_3$

$$\begin{aligned} &= \sqrt{(\cdot27629 - \cdot0955)^2 + (\cdot2500 + \cdot27629)^2 + (\cdot72371 - \cdot3455)^2} \\ &= \sqrt{(\cdot18079)^2 + (\cdot52629)^2 + (\cdot37821)^2} \\ &= \sqrt{(\cdot032685 + \cdot27698 + \cdot143042)} = \sqrt{\cdot452707} = \cdot67283. \end{aligned}$$

For finding  $B'''D_3$  :

The coordinates of  $B'''$  are  $-.3455, .0955, .25$  ;  
those of  $D_3$  are  $0, 0, 1$ .

Thus  $B'''D_3$

$$\begin{aligned} &= \sqrt{(\cdot3455)^2 + (-\cdot0955)^2 + (1 - \cdot25)^2} \\ &= \sqrt{\cdot11937 + \cdot00912 + \cdot56250} = \sqrt{\cdot69099} = \cdot83126. \end{aligned}$$

For finding  $A'B_1'''$  :

The coordinates of  $A'$  are  $-.0955, -.2500, +.3455$  ;  
those of  $B_1'''$  are  $+.6545, -.0955, +.7500$ .

Thus  $A'B_1'''$

$$\begin{aligned} &= \sqrt{(\cdot0955 + \cdot6545)^2 + (\cdot2500 - \cdot0955)^2 + (\cdot7500 - \cdot3455)^2} \\ &= \sqrt{(\cdot7500)^2 + (\cdot1545)^2 + (\cdot4045)^2} \\ &= \sqrt{\cdot5625 + \cdot02387 + \cdot16362} = \sqrt{\cdot7500} = \cdot86602. \end{aligned}$$

For finding  $A'C_2$  :

The coordinates of  $A'$  are  $-.0955, -.2500, +.3455$ ,  
those of  $C_2$  are  $+.72371, -.27629, +.27629$ .

Thus  $A'C_2$

$$\begin{aligned} &= \sqrt{(\cdot0955 + \cdot72371)^2 + (\cdot27629 - \cdot2500)^2 + (\cdot3455 - \cdot27629)^2} \\ &= \sqrt{(\cdot81921)^2 + (\cdot02629)^2 + \cdot06921^2} \\ &= \sqrt{\cdot67111 + \cdot00069 + \cdot00479} = \sqrt{\cdot67659} = \cdot82255. \end{aligned}$$

For finding  $C_2D_3$  :

The coordinates of  $C_2$  are  $+.72371, -.27629, +.27629$ ,  
those of  $D_3$  are  $0, 0, 1$ .

Thus  $C_2D_3$

$$= \sqrt{(\cdot72371)^2 + (\cdot27629)^2 + (\cdot72371)^2} \\ = \sqrt{2(\cdot52375) + \cdot076336} = \sqrt{1\cdot123836} = 1\cdot0601.$$

For finding  $B''D_3$  :

The coordinates of  $B''$  are  $+\cdot2500, -\cdot3455, \cdot0955$ ,  
those of  $D_3$  are  $0, 0, 1$ .

Thus  $B''D_3$

$$= \sqrt{(\cdot2500)^2 + (\cdot3455)^2 + (\cdot0945)^2} \\ = \sqrt{\cdot06250 + \cdot11937 + \cdot81812} = \sqrt{1} = 1.$$

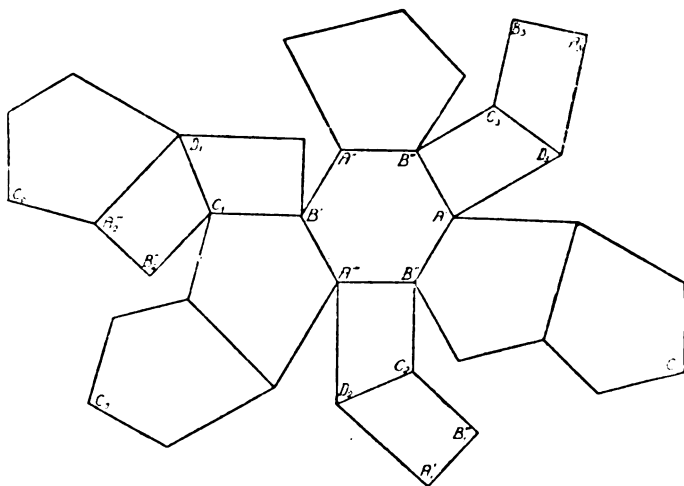
Finally, for finding  $B''B_1'''$  :

The coordinates of  $B''$  are  $+\cdot2500, -\cdot3455, \cdot0955$ ,  
those of  $B_1'''$  are  $+\cdot6545, -\cdot0955, \cdot7500$ .

Thus  $B''B_1'''$

$$= \sqrt{(\cdot4045)^2 + (\cdot2500)^2 + (\cdot6545)^2} \\ = \sqrt{\cdot16362 + \cdot06250 + \cdot42837} = \sqrt{\cdot65449} = \cdot8090.$$

Fig. 10.



E.

*Finally, as to the construction of a "mat."*

Fig. 9 (p. 951) shows the three kinds of cell faces derived from the foregoing ; and fig. 10 is a plan of the relative



situations of the 13 faces of a single cell as presented when they are hinged at their edges and folded down so as to lie in one plane.

A model of a cell is obtained from this plane diagram by transferring the arrangement shown to a sheet of cardboard and marking on this all the boundary lines of the faces as in fig. 10; then cutting half through the cardboard along all these lines and folding up the various polygons in such a way as to bring together lines representing the same edge. Selvages are left so as to attach corresponding boundaries securely. Cells of the two enantiomorphous forms are shown in fig. 3. The same "mat" serves for both enantiomorphous forms if the marking on the face of the diagram shows through at the back; the process employed at the face for the one form is similarly employed at the back for the other. This involves the mirror-image resemblance of the two forms.

The fitting of a number of the cells together so as to have no interstices is a simple matter if they are first paired so that the two cells of a pair have contact at their hexagonal faces, one being the image-mirror of the other, and the two being so adjusted as to be related by a centre of symmetry as shown in fig. 3, not by a plane of symmetry.

The author has called attention to the applicability of the space-partitioning here described to the case of a crystal of potassium chloride, the symmetry of which is regarded as hemihedral-cubic (Proc. Roy. Soc. A, vol. xci., 1914, p. 1). The geometrical representation given by him can be regarded as an extension of the method of graphic formulae employed by the organic chemist, undertaken for the purpose of representing crystal structure. The following points of resemblance between the artificial structure above described and the properties of the potassium chloride crystal are discernible:—

1. The similarity as to form and number of the two component enantiomorphous sets of cells renders them available for representing equality both of number and valency of the atoms of potassium and chlorine.
2. The cells form pairs, the enantiomorphous individuals of a pair being intimately and specially associated. A close attachment of two atoms, one of each kind, to form a molecule is thus pictured. The atomic arrangement according to a cubic lattice which has been previously suggested as the interpretation of the

experimental facts, fails in this respect since any choice of pairs of nearest points of this lattice to represent molecules is necessarily arbitrary and inconsistent with cubic symmetry.

3. The distances of the points found in the same skeleton cube from its centre being equal, the molecular centres are represented by the centres of half the skeleton cubes so selected as to be in edge-contact. This is the arrangement assigned by Bragg to the molecular centres.

The artificial system presents, however, if the allotment to the same kind of atom is uniform throughout, a lower class of symmetry than that assigned to the crystal, viz. tetartohedry not hemihedry. This discrepancy may be attributed to intimate twinning, which is capable of closely mimicking the higher class of symmetry.

Ewing's well-known experiment with a flock of freely suspended magnets is suggestive in connexion with the system described :—If magnets were freely suspended one in each pair of cells with its centre at the centre of the hexagonal interface separating them, their interaction might well produce stable equilibrium symmetrically related to the system of non-intersecting axes.

The foregoing is a particular case of an infinite series of partitionings each of which is based on some regular point-system the points of which form pairs, the two individual points of a pair lying within the same cubic cell of a half-system of cubic cells throughout which the cubes are in contact at edges only and being found on the same trigonal axis equidistant from the cell centre. The condition as to equality of joining lines differently related to the system which characterizes the particular case is absent in the other partitionings.

It is interesting to observe that the limiting cases between which the infinite series referred to lies are :—

( $\alpha$ ) That in which the two points of each pair lie precisely at opposite corners of a cubic cell on its non-intersecting trigonal axis; the point-system developed is a cubic space-lattice and the partitioning results in a regular system of cubic cells. If planes perpendicular to the trigonal axes and bisecting each line joining the points of a pair are added to the other bisecting planes, as in the instance given above, each cubic cell will be so bisected as to produce a hexagonal interface which is at right angles to its single non-intersecting

trigonal axis, and the two halves of a cell will be enantiomorphs and bear a mirror-image relation to each other.

( $\beta$ ) That in which the two points of each pair coalesce at the centre of a cubic cell of the half-system just referred to, thus constituting a face-centred cubic space lattice. The hexagonal faces here fall to zero and disappear and the cells are rhombic dodecahedra.

All of the infinite series except the two limiting cases present hemihedral cubic symmetry.

### XCIX. *On the X-Ray Spectra of Hafnium and Thulium.*

By D. COSTER \*.

[Plate XIII.]

**I**N a series of letters to 'Nature' † Hevesy and the present writer announced the discovery of the element of atomic number 72, and published some general data as regards the occurrence and chemical properties of this element, for which the name hafnium was proposed. It is the purpose of this note to give some more details about the physical methods used during our investigation. At the same time I am glad to use this occasion to complete the tables of wave-lengths of X-ray lines for the elements hafnium and thulium.

According to the Bohr theory of atomic structure ‡, the element of atomic number 72 must be homologous to titanium, zirconium, and thorium. As the elements in the neighbourhood of 72 (lanthanum, tantalum, tungsten) are very closely related to their homologues in the neighbourhood of zirconium (*i. e.*, yttrium, niobium, and molybdenum respectively), it seemed to be rational to expect that as regards its chemical properties the element 72 should be very closely related to zirconium, and that it eventually might be found in combination with this element. We therefore investigated the X-ray spectrum of zirconium minerals and of zirconium preparations, and we were able to prove that the substance ordinarily known as zirconium is not a pure element, but a mixture of two elements: for the greater part one of atomic number 40 and (usually in an amount of 1 to 5 per cent.) one of atomic number 72.

\* Communicated by Prof. N. Bohr.

† D. Coster and G. Hevesy, 'Nature,' vol. cxi. pp. 79, 182, 252, 462 (1923).

‡ See N. Bohr, 'Theory of Spectra and Atomic Constitution,' Cambridge, 1922.

During our investigations we used a vacuum spectrograph for relative measurements, constructed according to a design kindly furnished by Professor Siegbahn to this Institute. Using a Norwegian mineral, we were able to detect six lines of the L-series of the element 72. In Table I. are given our provisional results, which were published in 'Nature.' In the second column stand the values found by interpolation between the wave-lengths for the elements Cp (71) and Ta (73).

TABLE I.  
Provisional Results for the L-Series of Hafnium \*.

	Measured.	Interp.
$\alpha_2$ .....	1576	1576.9
$\alpha_1$ .....	1565.5	1565.9
$\beta_1$ .....	1371.4	1371.0
$\beta_3$ .....	1350.2	1349.5
$\beta_2$ .....	1323.7	1323.1
$\gamma_1$ .....	1677	1176.4

Not only was the agreement very close as regards the numerical values for the wave-lengths, but also the relative intensities of the different lines agreed with expectations. The presence of the element 72 in zirconium minerals and preparations was therefore established beyond all doubt. For the element 72 we proposed the name "hafnium," whereas it seemed to be reasonable to keep the name "zirconium" for the element of atomic number 40, which, in general, forms by far the greatest part of the zirconium as known before.

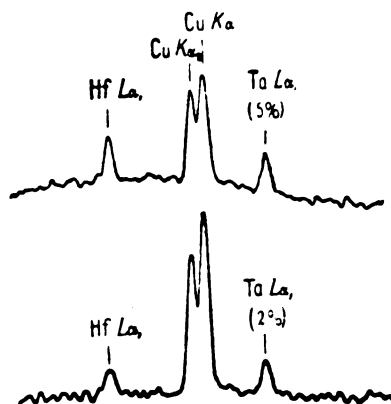
In order to get some idea about the concentration of hafnium in the different zirconium minerals and preparations, the following method was used. A known quantity of the element of atomic number 73 (tantalum) was added to the preparation, and an X-ray spectrum was taken of the mixture. By comparing the intensity of the hafnium lines with that of the corresponding tantalum lines, estimates of considerable accuracy were obtained as to the concentration of hafnium in the preparations. The reliability of this method follows from the same reasons that allow us to understand the great similarity of the X-ray spectra of different elements. Indeed, the X-ray lines are emitted during transition processes between stationary states by which electrons in the inner part of the atom take part,

\* Cf. 'Nature,' vol. cxi. p. 79 (1923).

and the conditions at the outside of the atom have no appreciable influence on these processes. We may therefore expect that the intensity of X-ray lines is simply proportional to the number of atoms present in the anticathode spot\*.

The method is illustrated by figs. 1, 2, and 3. They are photometer curves obtained by measurements of the plates with a Moll photometer. Fig. 1 relates to the investigation

Fig. 1.



of zirconium minerals. The upper curve on this figure is taken from a Ural zirconium mineral, the lower from a Brazil mineral. The first mineral seems to contain about 5 per cent. Hf, the other a little less than 2 per cent. Fig. 2 shows how the chemical properties of hafnium were studied. A solution of a mixture of zirconium and hafnium in strong acids was precipitated with sodium phosphate in eleven subsequent fractions, each containing the same amount of insoluble phosphate. To every fraction 10 per cent. of tantalum was added. The curve at the top is taken from the spectrum of the first fraction, the next curve from the fourth fraction, and the bottom curve from the eighth fraction. We may conclude from these curves that hafnium phosphate is even less soluble than zirconium phosphate. Figure 3 gives a control to the method. Two artificial preparations were made by adding  $\text{SnCl}_2$  and  $\text{Sb}_2\text{O}_3$  to calcium phosphate. Both preparations contained 10 per cent.

\* For a closer discussion of the matter, see D. Coster, *Chemical News*, vol. cxxvii, p. 65 (1923).

Fig. 2.

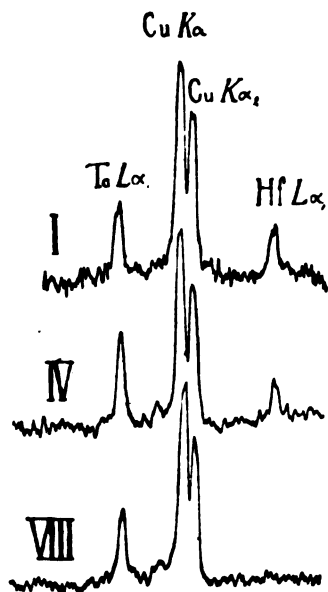
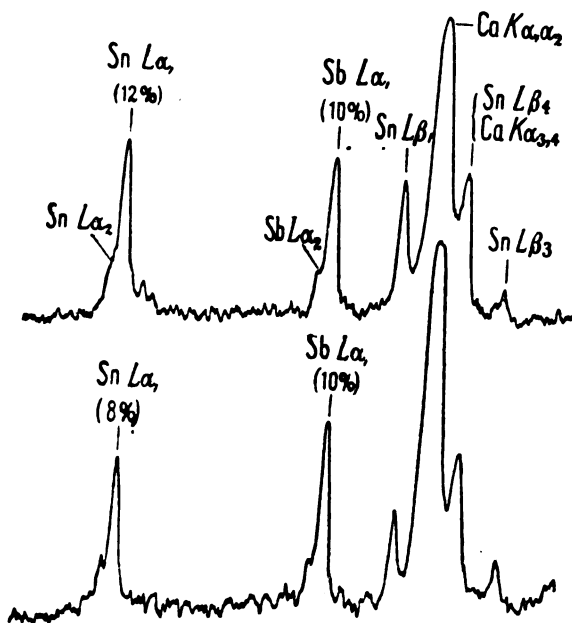


Fig. 3.



antimony, whereas 12 per cent. tin was added to the first fraction and 8 per cent. tin to the second fraction. The curves actually show that the amount of antimony in the first case is smaller and in the second case larger than the amount of tin present in the preparation.

With the aid of methods described by Hevesy\*, hafnium preparations were obtained which contained only small amounts of zirconium (less than 5 per cent.). One of these preparations was used to take strongly-exposed X-ray spectra with calcite as analysing crystal throughout the whole region of the L-series. Besides, some lines of the M-series were exposed, using gypsum as analysing crystal. The wavelengths measured from these plates are given in Table II.

TABLE II.  
L-Series of Hafnium.  
*Emission Spectrum.*

Line.	Glancing angle, Calcite.	$\lambda$ .	$\frac{\nu}{R}$ .	$\sqrt{\frac{\nu}{R}}$ .
<i>l</i> .....	17° 3' 39"	1777.4	512.70	22.643
<i>a</i> <sub>2</sub> .....	15° 5' 21"	1577.04	577.84	21.038
<i>a</i> <sub>1</sub> .....	14° 58' 54"	1566.07	581.89	24.125
<i>η</i> .....	14° 31' 40"	1519.7	599.66	24.488
<i>β</i> <sub>4</sub> <sup>1</sup> .....	13° 15' 28"	1389.3	655.91	25.611
<i>β</i> <sub>1</sub> - <i>β</i> <sub>6</sub> ...	13° 4' 53"	1371.1	664.60	25.780
<i>β</i> <sub>3</sub> .....	12° 52' 22"	1349.7	675.20	25.985
<i>β</i> <sub>2</sub> .....	12° 37' 10"	1323.5	688.51	26.238
<i>β</i> <sub>7</sub> .....	12° 25' 33"	1303.5	699.08	26.440
<i>γ</i> <sub>5</sub> .....	11° 32' 31"	1212.1	751.80	27.419
<i>γ</i> <sub>1</sub> .....	11° 11' 54"	1176.5	774.55	27.831
<i>γ</i> <sub>2</sub> .....	10° 51' 32"	1141.3	798.46	28.257
<i>γ</i> <sub>3</sub> .....	10° 48' 16"	1135.6	802.48	28.328
<i>γ</i> <sub>4</sub> .....	10° 27' 47"	1100.1	827.68	28.769

<sup>1</sup> Confounds with K $\beta$ <sub>1</sub> of Cu.

The lines L $\alpha$ <sub>1</sub> and L $\alpha$ <sub>2</sub> were determined by Mr. Hjalmar in the laboratory of Professor Siegbahn, using a spectrograph for absolute measurements with the aid of a hafnium preparation provided by us. His results were kindly put at our disposal. They agree very well with the results obtained by Mr. Žaček in the same laboratory †. The error in the wavelengths of these lines is less than 0.1 X-unit. The other

\* G. Hevesy, *Chemische Berichte*, lvi., p. 1503 (1923); *Chemical News*, cxxvii. p. 33 (1923).

† *Zs. für Phys.* vol. xv. p. 31 (1923).

TABLE III.

## L-Series of Hafnium.

*Absorption Spectrum.*

Limit.	Glancing angle, Calcite.	$\lambda$ .	$\frac{\nu}{R}$ .	$\sqrt{\frac{\nu}{R}}$ .
$L_I^1$ .....	10 25 ' 7	1097	830.70	28.822
$L_{II}$ .....	10 57 28	1151.5	791.37	28.131
$L_{III}$ .....	12 19 25	1293.0	704.77	26.547

<sup>1</sup> Confounds with  $L_{\gamma_1}$  of W.

TABLE IV.

## M-Series of Hafnium.

Line.	Glancing angle, Gypsum.	$\lambda$ .	$\frac{\nu}{R}$ .	$\sqrt{\frac{\nu}{R}}$ .
$\alpha$ .....	29 45 ' 6	7521	121.15	11.008
$\beta$ .....	28 44 19	7236	125.06	11.183

lines in the L-series were measured relatively to the  $\alpha$ -lines or to the copper or tungsten lines appearing on the same plates. Here the error will be in most cases less than 0.4 X-units. The wave-lengths of the lines of the M-series which were determined with a gypsum crystal are less accurate. Here the error may be of the order of magnitude of 2 X-units. Plate XIII. gives the reproduction of most of the lines in the L-series. The lines  $\gamma_4$  and  $l$  lie outside the region exposed. The copper lines are due to the copper of the anticathode, the tungsten lines are due to the tungsten sputtered by the hot wire.

Besides the lines and absorption limits given in Table II., also the K-absorption limit of hafnium is known. This was measured by de Broglie and Caprera\* shortly after our discovery of the presence of the element 72 in zirconium minerals was announced. In their investigation de Broglie and Caprera used as absorbing substance a zirconium mineral which obviously contained a rather high percentage of hafnium. They found the value 190.5 X-units.

It might be of some interest to discuss the question of how to identify the two X-ray lines found by Dauvillier† in a preparation of rare-earth metals and ascribed to a rare-earth element celtium, the presence of which in this preparation

\* *Comptes Rendus*, vol. clxxvi. p. 433 (1923).† *Comptes Rendus*, vol. clxxiv. p. 1347 (1922).



was suspected by Urbain. The wave-lengths given by Dauvillier for these lines are 1561·8 and 1319·4 X-units respectively. The differences between these wave-lengths and those given in Table II. for the hafnium lines  $L_{\alpha 1}$  and  $L_{\beta 2}$  are 4·3 and 4·1 X-units respectively, which correspond to distances on Dauvillier's plates of about 0·7 mm., 1 mm. corresponding to 6 X-units. The wave-lengths of the lines of the elements Yb and Cp found by Dauvillier on the same plates on which the cerium lines were detected, however, agree closely with those found by the writer. If in the special case of the Ct lines we accept differences of 4·3 X-units between the precision measurements from Siegbahn's laboratory and Dauvillier's measurements, we get the following other possibilities for the identification of the same lines :—

1561·8 : 2nd order	Zr- $K_{\alpha 1}$ , Sr- $K_{\beta 1}$ ,
3rd	„ Pd- $K_{\beta 1}$ ,
4th	„ Ba- $K_{\alpha 2}$ , I- $K_{\beta 1}$ ;
1319·4 : 1st	„ Pt- $L_{\alpha 2}$ , Ta- $L_{\beta 1}$ ,
3rd	„ I- $K_{\alpha 2}$ ,
4th	„ Nd- $K_{\alpha 1}$ .

None of these possibilities were discussed in Dauvillier's original paper \*.

Identifying, however, Dauvillier's lines with lines of the element 72, we meet with the following difficulties. If the line 1319·4 should be  $L_{\beta 2}$  of hafnium, it is difficult to see why the line  $\beta_1$  of the same element, which is stronger, was not visible on Dauvillier's plate †. Besides, the line 1561·8 which should be identifiable with Hf  $L_{\alpha 1}$  was, according to Dauvillier, so faint that it was on the limit of visibility. In this case, however, it is scarcely probable that the much less intense line  $L_{\beta 2}$  of the same element should be visible at all.

In a former paper ‡, I gave the results of the measurements

\* *Comptes Rendus*, vol. clxxiv. p. 1347 (1922). In a later discussion of our results as regards the identification of the element 72, however, Dauvillier (*Comptes Rendus*, vol. clxxvi. p. 676 (1923)) discusses the possibilities Ta, Zr, Pd, Ba, Nd, but not Pt, Sr, or I.

† A photograph taken of a mixture of the elements Hf and Cp showed that the line Hf  $L_{\beta 1}$  does not coincide with any Cp-line as was thought by Dauvillier. The lines Hf  $L_{\beta 1}$  and Cp  $L_{\beta 2}$  lie at a distance of more than 4 X-units from one another, which is nearly the same distance as the distance of the two copper lines  $K_{\alpha 1}$  and  $K_{\alpha 2}$  on Plate XIII., whereas the satellite which Dauvillier found at a distance of 1 X-unit from Cp  $L_{\beta 2}$  and which he calls Cp  $L_{\beta 2}'$  could not be detected by us even on a very strongly exposed plate.

‡ Phil. Mag. xlv. p. 546 (1922).

of the lines in the L-series of all the elements from La to Cp, with the exception of those with atomic numbers 61 and 69. The element 61 is unknown, while 69 is usually identified with the rare-earth element thulium, which possesses an atomic weight between that of Er (68) and that of Yb (70). In the spectrum of the same Yb-Cp preparation of Urbain, in which Dauvillier found the two lines ascribed to the element 72, he also detected three very weak lines which he identified with the lines  $\beta_2$ ,  $\gamma_1$  and  $\gamma_2$  of the element of atomic number 69. The amount of the element 69 in Dauvillier's preparation, however, was very small, and no direct evidence was obtained as to whether this element is the same as the element thulium, known by its optical spectrum and chemical properties. Therefore I have undertaken an investigation of a concentrated thulium preparation kindly put at our disposal by Dr. Auer von Welsbach. The X-ray spectrum showed that this preparation actually consisted almost entirely of the element of atomic number 69. Also the presence of a little ytterbium and of a trace of erbium could be detected. The results of the measurements are given in Table V.

TABLE V.  
L-Series of Thulium.

Line.	Glancing angle, Calcite.	$\lambda$ .	$\frac{\nu}{R}$ .	$\sqrt{\frac{\nu}{R}}$ .
$\lambda$ .....	18 47 19	1951.1	467.05	21.611
$a_2$ .....	16 36 36	1733.9	525.57	22.926
$a_1$ .....	16 31 24	1722.8	528.93	22.998
$\eta$ .....	16 12 21	1692.3	538.49	23.212
$\beta_4^1$ .....	14 44 17	1541.2	591.26	24.316
$\beta_1$ .....	14 35 53	1526.8	596.84	24.431
$\beta_6$ .....	14 26 53	1511.5	602.90	24.554
$\beta_3$ .....	11 21 28	1502.3	606.60	24.629
$\beta_2$ .....	13 56 51	1460.2	624.10	24.982
$\gamma_5$ .....	12 53 54	1352.3	673.88	25.959
$\gamma_1$ .....	12 30 50	1312.7	694.23	26.348
$\gamma_2$ .....	12 6 48	1271.2	716.83	26.291
$\gamma_3^2$ .....	12 3 20	1265.3	720.22	26.837
$\gamma_4^3$ .....	11 40 47	1226.4	743.03	27.259

<sup>1</sup> Coincides with  $Ka_2$  of Cu.

<sup>2</sup> Coincides with  $L_{\gamma_1}$  of Yb.

<sup>3</sup> Coincides with  $L_{\gamma_3}$  of Yb.

Institute for Theoretical Physics,  
Copenhagen,  
August 1923.

*C. The Stark Effect for Strong Magnetic Fields.**To the Editors of the Philosophical Magazine.*

GENTLEMEN,—

ON the pages of your esteemed Magazine there has recently appeared an argument on the above subject between Messrs. A. M. Mosharrafa (xliii. p. 493; xlv. p. 371, 1922) and H. O. Newbould (xlv. pp. 1081, 1923), resulting in a discrepancy of opinions between them. Both those authors seem not to have been familiar with the writer's earlier work on the same subject. In fact, the term of the Stark effect depending on the square of the electric force was computed and published by myself several years ago (*Annalen d. Physik*, li. p. 184, 1916). My formula is identical with that given last year by Mosharrafa, and therefore in disagreement with Newbould's result. After the appearance of his paper I checked my computations and confirmed them.

Permit me to add that Mr. Takamine's interesting observations on the Stark effect in strong fields were discussed before Mosharrafa by Sommerfeld (*Annalen d. Physik*, 1920), who pointed out that they can be accounted for by my formula.

PAUL S. EPSTEIN.

Norman Bridge Laboratory of Physics,  
Pasadena (Calif.), June 6th, 1923.

CI. *The Electronic Theory of Valency.*—Part II. *Intramolecular Ionization in Organic Compounds.* By Professor T. MARTIN LOWRY, C.B.E., M.A., D.Sc., F.R.S.\*

1. *Intramolecular Ionization in Inorganic Compounds.*

IN the preceding paper of this series † I directed attention to the fact that the electronic theory of valency permits of a very wide extension of Thomson's theory of intramolecular ionization, and that polar bonds may be detected in a large range of inorganic compounds where it has been generally assumed hitherto that the linkages are all of a

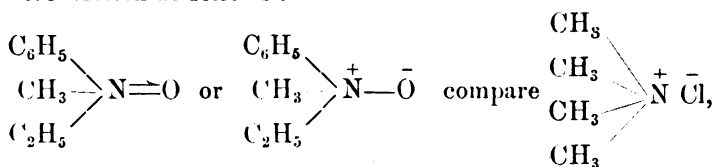
\* Communicated by the Faraday Society.

† Trans. Faraday Soc. xviii. p. 285 (1923); Phil. Mag. [6] xlv. p. 1105 (1923).

non-polar or covalent type. In particular, a study of the electronic formulæ of Langmuir reveals the fact that, whilst there is usually a perfect balance between the nuclear charge of each atom and the enveloping shell of electrons, in other cases the negative charge of the shell is either too large or too small to balance exactly the positive charge of the nucleus. Thus, in the case of  $\text{CO}_2$  and  $\text{N}_2\text{O}$  (adopting Lewis's symbols for the double bonds), the analysis of the charges works out as follows :—

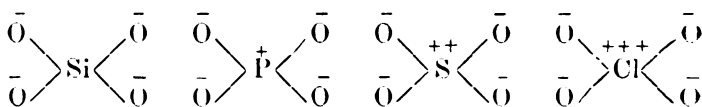
	$\ddot{\text{O}}:$	$:\text{C}:$	$\ddot{\text{O}}:$	$\ddot{\text{O}}:$	$:\text{N}:$	$\ddot{\text{N}}:$
K-electrons ... ..	2	2	2	2	2	2
L-electrons,						
shared ( $\div 2$ ) ...	2	4	2	2	4	2
unshared.....	4	0	4	4	0	4
Total electrons ...	8	6	8	8	6	8
Nuclear charge ...	8	6	8	8	7	7
Resultant charge .	0	0	0	0	+1	-1

The residual charges thus detected in Langmuir's formula for nitrous oxide were represented by writing the compound as  $\text{O}=\text{N}^+=\bar{\text{N}}$  or  $\text{O}=\text{N}^+\equiv\bar{\text{N}}$ , where the barb represents an electrovalency passing from the positively to the negatively charged atom\*. Intramolecular ionization was also detected in Langmuir's formulæ for the amine oxides, which were written as follows :—



\* This formula for nitrous oxide shows the active bond as joining two nitrogen atoms. The behaviour of the gas is, however, much more like that of an oxide of  $\text{N}_2$ , reacting in the form  $\bar{\text{O}}-\text{N}^+\equiv\text{N}$ , although the familiar ring-formula  $\begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{N} \end{array} \text{O}$  is also a possible alternative as a picture of the molecule in its resting phase. The argument from isosterism may be met by pointing out that benzene and thiophen, which do not even contain the same number of atoms or of planetary electrons, resemble one another even more closely than do  $\text{CO}_2$  and  $\text{N}_2\text{O}$ .

and for the ions of the oxy-acids  $\text{H}_4\text{SiO}_4$ ,  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{HClO}_4$ , which were written as



## 2. Application to Organic Compounds.

An extensive application of the theory of intramolecular ionization to organic compounds is rendered possible by taking advantage of a more recent conception of Sir J. J. Thomson. He suggests that the reactivity of double bonds in organic chemistry may be attributed to the fact that it is easier to open the hinge between two cubical octets sharing a common face\* than to break the hinge which holds together two octets sharing only a common edge. This view can scarcely be accepted as an adequate explanation of the reactivity of double bonds, since fluorine is in fact far more reactive than oxygen; but if the assumption be made that the rupture of the double bond takes place unsymmetrically, so as to leave 8 L-electrons on one atom and only 6 on the other†, a very suggestive system of formulæ is arrived at, in which ethylene is represented as containing a "mixed double bond," whilst acetylene can be represented in a similar way as containing a "mixed triple bond." These formulæ may be analysed, just as in the case of Langmuir's formulæ for  $\text{CO}_2$  and  $\text{N}_2\text{O}$ , as follows:—

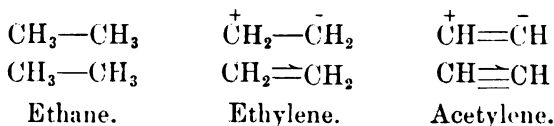
	<i>Ethane.</i>		<i>Ethylene.</i>		<i>Acetylene.</i>	
	$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ \text{H} : \ddot{\text{C}} : \ddot{\text{C}} : \text{H} \\   \quad   \\ \text{H} \quad \text{H} \end{array}$		$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ \text{H} : \ddot{\text{C}} : \ddot{\text{C}} : \text{H} \\   \quad   \\ \text{H} \quad \text{H} \end{array}$		$\begin{array}{c} \text{H} : \text{C} : \ddot{\text{C}} : \text{H} \end{array}$	
K-electrons .....	2	2	2	2	2	2
L-electrons						
shared ( $\div 2$ ) ...	4	4	3	3	3	3
unshared .....	0	0	0	2	0	2
Total electrons ...	6	6	5	7	5	7
Nuclear charge ...	6	6	6	6	6	6
Resultant charge ..	0	0	+1	-1	+1	-1

In view of the electric charges which are disclosed by this

\* Compare Lewis, J. A. C. S. xxxviii. p. 778 (1916).

† Compare Lewis's view of the dissociation of the diatomic molecule of a halogen into an octet and a sextet, *loc. cit.* p. 775.

analysis, these formulæ may be written in a conventional form as follows :—



A large number of organic compounds have been formulated on these lines in a paper on "The Polarity of Double Bonds," which has recently appeared in the *Journal of the Chemical Society* \*. These formulæ may be regarded, from one point of view, as merely introducing a uniform nomenclature to express a number of phenomena in organic chemistry which cannot be represented satisfactorily by Kekulé's non-polar or covalent bond. Hitherto it has been the rule to introduce a new nomenclature and a new symbolism to express each anomaly as it has been encountered, *e.g.* centric bonds in aromatic compounds, carbonium bonds, mobile hydrogen atoms, residual affinities, partial valencies, principal and subsidiary valencies, etc. Most of these anomalies can now be recognized as being due to the development of electrovalencies and a single symbolism may be used to express them all. The time is indeed ripe for chemists to state definitely how many types of valency they require the physicist to provide, and, in particular, whether in organic chemistry the non-polar tetrahedrally-arranged bonds of diamond, giving a distance of 1.5 Ångström units between the centres of adjacent carbon atoms, and the electrovalent link † with its radiating fields of electrostatic force, are sufficient to express the facts of chemical combination, or whether these must be supplemented by half-a-dozen more types of linkage to cover special cases and anomalies.

The introduction of a uniform nomenclature and symbolism has, however, had the further effect of disclosing relationships between a number of phenomena which have hitherto appeared to be entirely independent of one another. Thus, reactivity in organic chemistry can now be ascribed to the same cause as reactivity in inorganic chemistry, namely to a process of ionization, although the ions in organic chemistry are usually "bound" instead of "free." Again, the theory of "crossed polarities," which follows directly from the symbolism now suggested, makes it possible to ascribe to a

\* *Trans. Chem. Soc.* cxxiii. p. 822 (1923).

† This appears to give a distance between centres of 3.25 Å.U. in graphite.

common cause a series of chemical changes, in derivatives of maleic acid and of benzene respectively, which have hitherto been discussed separately, if discussed at all. In the same way, the theory of "multipolar ions" has disclosed a wholly unexpected relationship between the phenomena of dynamic isomerism and those of coordination. These correlations are of interest on general grounds; but their real value lies in the large amount of experimental work which they have already suggested.

### 3. *Reactivity and Activation of Organic Compounds.*

In describing to the Chemical Society\* some of the consequences that follow from the theory that "a double bond in organic chemistry usually reacts as if it contained one covalency and one electrovalency," I laid considerable stress on the fact that the resting states of the molecule are not necessarily identical with their reactive phases. It is, therefore, not necessary to assume that a polar double bond always represents the most stable form of an unsaturated compound, nor that a "hinge" when once opened is incapable of closing up again.

The idea that many types of molecules undergo a preliminary process of activation before undergoing chemical change is an old one, and has been developed very largely by Arrhenius; but this idea has hitherto been mainly physical in character, since the problem has usually been studied from the standpoint of the amount of energy (*e.g.* the number of quanta of radiation) required to effect the activation, rather than of the chemical character of the processes involved. The views which are now put forward make it possible to assign, however, a definite chemical meaning to the process of activation, since it appears that in many cases this may consist simply in the conversion of covalent into electrovalent bonds. This is in accordance with the generally-recognized fact that ions will interact immediately without any preliminary process of activation. A very wide field of experimental research is thus opened out, and, if the views in question should prove to be well-founded, it will be possible to revive in a modern electronic form the theory of Armstrong that "chemical action is reversed electrolysis," since it would appear that "chemical action is ultimately an action between ions, either free or bound." The physico-chemical aspects of the theory of intramolecular ionization may therefore prove to be not less fertile than the purely chemical aspects.

\* Trans. Chem. Soc. cxxiii. p. 822 (1923).

## 4. Polar Organic Compounds.

It is probable that organic compounds may be divided into two groups according as the normal structure of the molecule is polar and therefore reactive, or is non-polar and must undergo isomeric change into a polar form before it can react. Some examples of molecules which may be permanently polar are set out in the following paragraphs.

(a) *Organo-metallic Compounds*.—According to the electronic theory of valency, the lighter metals are only stable in the condition of ions; and the bonds which unite them to other elements are always of the nature of electrovalencies\*. If this view be accepted, the metallic derivatives of organic radicles must all have a polar structure like that assigned to sodium chloride,  $\text{Na}^+\text{Cl}^-$ . From this point of view, zinc

methyl,  $\text{Zn}^+ \begin{array}{c} \text{CH}_3 \\ \diagup \quad \diagdown \\ \text{CH}_3 \end{array}$ , and the Grignard reagent,  $\text{Mg}^+ \begin{array}{c} \text{CH}_3 \\ \diagup \quad \diagdown \\ \text{I} \end{array}$ ,

should exist only in a polar form, in which the methyl-groups are present as anions linked to the metallic kation by electrostatic forces. This does not mean that these compounds must necessarily yield conducting solutions, since it must be remembered that an ionizing solvent is generally required in order to enable the ions to separate to such a distance that they can move in opposite directions under the influence of electrostatic forces, instead of clinging together, *e. g.* as an electrically-neutral doublet. Failing the discovery of a suitable ionizing solvent, experiments on the ionization-potentials of the vapours of some of these metallic compounds would be of great interest.

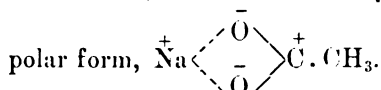
(b) *Metallic Salts*.—Similar considerations apply in the case of metallic derivatives of a more commonplace character, such as sodium ethoxide,  $\text{Na}^+\text{O}^-\text{C}_2\text{H}_5$ , sodium phenate,  $\text{Na}^+\text{O}^-\text{C}_6\text{H}_5$ , or sodium acetate,  $\text{Na}^+\text{O}^-\text{CO}.\text{CH}_3$ . In the first of these compounds, the radicle attached to the oxygen atom of the anion is saturated, and there is no reason to suppose that this can easily assume a polar character; although, if a rupture were actually to take place between oxygen and carbon or between carbon and carbon, it is probable that the general rule would be followed that under these conditions a covalency gives rise to an electrovalency,

\* The heavier metals, on the other hand, may be covalent in their coordination-compounds.



*i. e.* to a sextet and an octet rather than to two septets. On the other hand, in sodium phenate and sodium acetate, the radicle attached to the oxygen is unsaturated in the sense that it is commonly represented as containing one or more "double bonds." These double bonds can be pictured as capable of changing over into a polar form and, although it may be difficult to provide absolute proof, it is reasonable to

suppose that the polarity of the  $\text{Na}\bar{\text{O}}^+$  group may be transmitted to the remainder of the conjugated system and that, for instance, sodium acetate may normally exist in the fully-



(c) *Quinquevalent Nitrogen as a Key-atom.*—From the considerations set out above it will be seen that the metals may play a very important part as "key-atoms" in maintaining the "induced alternated polarities" of a conjugated molecule\*. A similar part may sometimes be assigned to oxygen in view of the limitation, which is generally assumed to be inherent in the octet theory, of the number of covalencies to four in the case of elements of small atomic number. I have already quoted in a note to the Chemical Society the

case of methylethylaniline oxide,  $\text{C}_6\text{H}_5 \cdot \text{N}^+ \text{McEt} \cdot \bar{\text{O}}$ , where a reversion of the double bond between nitrogen and oxygen to a non-polar form would involve the production of a quinquevalent atom of nitrogen; in that case I have suggested that the double bond may be permanently polar in character, and that the nitrogen must always carry a positive charge, just as in the commoner ammonium salts, such as ammonium

chloride,  $\text{NH}_4^+ \text{Cl}^-$ . Similar considerations suggest that the

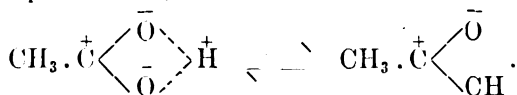
nitro-group, which I have written as  $\bar{\text{O}} - \text{N}^{++} - \bar{\text{O}}$ , is incapable of assuming the non-polar condition indicated by the formula  $\text{O} = \text{N} = \text{O}$ , although it might very well assume the cyclic

form  $-\text{N} \begin{array}{c} \diagup \text{O} \diagdown \\ | \\ \text{O} \end{array}$ . Under these conditions the nitro-group

may sometimes act (like ammonium) as a key-radicle in maintaining the polarity of a conjugated system; the action of nitro-groups in stabilizing the structure of benzene is indeed already recognized.

\* Compare Lapworth, 'Manchester Memoirs,' lxiv. no. 2, p. 1 (1920); Trans. Chem. Soc. cxxi. p. 417 (1922).

(d) *Other Key-atoms.*—There is good reason for thinking that ionizable chlorine and ionizable hydrogen may also act as key-atoms in fixing the polarity of a conjugated system. This action is, however, less certain since chlorine and hydrogen are both capable of forming covalent bonds, and can therefore readily pass into a non-ionized form. Thus, if Hantzsch's views of the relationship between the fatty acids and their salts and esters are correct, a fatty acid in aqueous solution may be formulated as an equilibrium-mixture of true acid and pseudo-acid, thus



The ionization, which is permanent in the salts, may therefore be only temporary in the acid from which they are derived. It is, moreover, possible that, when the acidic hydrogen atom passes over from the coordinated to the hydroxylic form, the carbonyl group may also become non-polar, although I do not know of any experimental data by which this point can be decided.

### 5. *Non-polar Organic Compounds.*

(i.) It must be recognized that in general all fully saturated compounds are non-polar unless ionizable. Thus, an electrovalency can only be developed, in a system made up entirely of single bonds, by breaking one of the covalencies, and so producing two independent ions, instead of the bound ions that are formed by the rupture of the double bond. The reactivity of a saturated compound probably depends on the readiness with which this conversion of a covalency into an electrovalency can occur. In the same way the reactivity of an "unsaturated" compound may be measured by the readiness with which a double covalency can be converted into a "mixed double bond." In many cases this conversion is very difficult to effect; thus oxygen gas (although it contains a double bond and is capable of forming addition-compounds, *e.g.* with hydrogen gas) is not usually classed as unsaturated, since it is very inert and requires to be activated, *e.g.* by heat or by a catalyst, before it will unite with other elements, although it will unite in the cold with nitric oxide. In general it may be said that a compound which requires "activating" before it will react is probably in a non-polar condition, whilst instant reactivity suggests that the compound is already ionized, whether the ions are free or bound.

(ii.) In the absence of a metallic ion or other powerful key-atom there is no guarantee that the polar condition of the molecule will be maintained in its resting state. In the case of ethylene, although the polar formula clearly represents in a most effective way the mechanism of the interaction of the unsaturated hydrocarbon with ionizable reagents, definite evidence is now available to show that the hydrocarbon itself is inert. Thus, Stewart and Edlund, by investigating the rate of reaction between ethylene and bromine\*, have established the fact that "reaction takes place for the most part, if not entirely, on the walls of the containing vessel," and "no evidence of gaseous reaction could be found." These conditions are very similar to those which prevail in the case of oxygen and hydrogen which, even when moist, will only react at atmospheric temperatures when in presence of a catalyst.

(iii.) The problem of deciding whether in other cases the resting form of the molecule is active or inactive is obviously one that must be settled by experiment, not by guessing, since there are at present not sufficient data to make it possible to establish any general rule. The observations of Stewart and Edlund are, however, sufficient to justify the view that the homologues of ethylene probably pass into a polar form only during chemical change; this renders possible a simpler explanation of their behaviour towards reagents than would be possible if the polar molecules represented the resting-state of the hydrocarbon. For instance, the production of by-products may be due, not to the reversal of an existing polarity, but to the double bond becoming polar in opposite senses to an extent which varies with the degree of polarity of the reagent. Thus propylene gives †

with HCl..... 99½ % of  $\text{CH}_3\cdot\text{CHCl}\cdot\text{CH}_3$  to ½ % of  $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_2\text{I}$ ;

with ICl ... 75 % of  $\text{CH}_3\cdot\text{CHCl}\cdot\text{CH}_2\text{I}$  to 25 % of  $\text{CH}_3\cdot\text{CHI}\cdot\text{CH}_2\text{Cl}$ ;

with BrCl... 58 % of  $\text{CH}_3\cdot\text{CHCl}\cdot\text{CH}_2\text{Br}$  to 42 % of  $\text{CH}_3\cdot\text{CHBr}\cdot\text{CH}_2\text{Cl}$ .

### 6. Conjugation and Crossed Polarities.

(a) The theory of mixed double bonds gives a new interpretation to the phenomena of conjugation discussed by Thiele in 1899. It now appears that a conjugated compound is one which, in its reactive form, contains an unbroken series

\* J. Amer. Chem. Soc. xlv. p. 1014 (1923).

† Michael, *J. prakt. Chem.* [2] lx. p. 445 (1899); *Ber.* xxxix. p. 2140 (1906).

of positive and negative charges on alternate atoms. This view differs fundamentally from Thiele's original conception, in that, whereas he chooses maleic acid as a typical example of conjugation, the new theory shows in this compound a discordant series of polarities, which destroys the conjugation of the system. On this point a definite experimental test of the theory can be made, since, if Thiele's view were correct, the maleic type of structure should be particularly stable, whilst in the light of the present theory the crossed polarities would render it relatively unstable, at least under conditions which tend to promote polarization of the molecule. I have already\* directed attention to three cases in which derivatives of maleic acid get rid of this condition of crossed polarities by undergoing isomeric change to a compound in which the series of alternate single and double bonds is shorter, but in which the polarities are no longer discordant; I also quoted one case† in which the crossed polarities are rendered concordant by the loss of a molecule of carbon dioxide. In another group of cases, which has been studied intensively by Thorpe and his colleagues‡, the crossed polarities are eliminated by the addition of water or of ethyl alcohol. In the absence of any alternative explanation of these changes, and especially in view of the fact that Thiele's views lead to a directly opposite conclusion, the series of cases quoted above may be regarded as decisive evidence in favour of the theory of polar double bonds.

(b) It is also of interest to notice the conditions under which these changes occur. Loss of carbon dioxide and gain of water and alcohol actually occur during the course of reactions carried out with a view to preparing acids of a maleic type; it is therefore likely that these changes take place whilst the molecule is in the reactive or polar form. When, however, a compound of a maleic type has been isolated, the isomeric changes that have been referred to above are brought about by boiling with strong caustic soda, *i.e.* under the very conditions that have been postulated (p. 970) as likely to drive a molecule over into a polar form. Opposite conditions can be achieved by converting the acid into its anhydride, since this not merely removes the sodium ions of the salt but also eliminates even the acidic hydrogen of the acid. All possibility of forming free ions is thus removed and, in the absence of these ionizable key-atoms, it is

\* Trans. Chem. Soc. cxxiii. p. 825 (1923).

† *Ibid.*

‡ Trans. Chem. Soc. cxi. p. 650 (1922).

doubtful whether even the polarity of the carbonyl groups would be maintained. It is precisely under these conditions that a double bond, which has been expelled from its original position under the influence of caustic soda, creeps back again into the ring and yields a derivative of maleic anhydride.

(c) A number of other cases are known in which strong caustic soda is used to bring about chemical or physical changes, *e. g.* a reversal of sign in the rotatory power of the tartrates. It will be of interest to inquire whether in these cases also the chemical changes demand the formation of a polarized molecule as an intermediate or final product, and whether the physical properties developed by the soda are those that might be expected in a molecule of this kind.

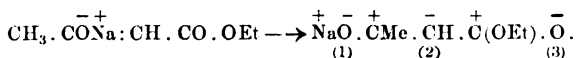
(d) In a totally different field crossed polarities afford a simple explanation of the mobility of aromatic groups which are "incorrectly" oriented, *e. g.* the *meta* nitro-group of  $\beta$  and  $\gamma$  trinitrotoluene. Apart from the theory of induced polarity, it is difficult to see any clear reason why nitro-groups occupying adjacent positions in the benzene ring should be so mutually antagonistic.

### 7. Multipolar Ions.

An important application of the theory of mixed double bonds is found in the discovery of the multipolar ion, *i. e.* of ions which, in addition to the electrification which is required to give the net charge of the ion, possess a series of additional positive and negative charges, so that, for instance, a univalent anion may contain *three* negatively charged atoms, alternating with *two* positively charged atoms, giving the net charge of minus *one*. This discovery has provided a novel interpretation of the phenomenon of tautomerism, and has disclosed a relationship between tautomerism and coordination which appears not to have been recognized previously, even by those who were working on these two phenomena separately, since no definite liaison had been established between these two independent lines of investigation.

(a) *Tautomeric Ions*.—It has usually been assumed that ethylacetoacetate can yield two ions, one derived from the ketonic form of the ester, and the other from the enolic form; and that the reversible isomeric change of the esters (which appears to demand the presence of a trace of an alkaline catalyst) involves both the migration of a mobile hydrogen ion and a structural rearrangement of the anion.

If, however, the views set out in paragraph 4 (*b*) above are adopted, it would appear that, in the sodium derivative at least, the metallic atom may act as the key-atom in setting up "induced alternating polarities" throughout the conjugated chain, as shown in the following scheme\* :—



The ion of the ester is now seen to contain three negative poles. It is tautomeric, since if a hydrogen ion be attached to the negative pole 2 it will yield a ketone, whilst if attached to the negative pole 1 it will yield an enol having the formula conventionally assigned to this compound; if attached to the negative pole 3 it would yield an isomeric enol, in which the carboxyl-group instead of the ketonic-group has been enolized.

No evidence of the existence of a second enol has been discovered, and of this fact also the electronic theory provides a simple explanation, which I have discussed in a paper on "Coordinated Hydrogen" recently communicated to the Chemical Society†. This explanation is based on the assumption that in the sodium-derivative, a sodium ion is coordinated with two oxygen poles 1 and 3 in just the same way as in the metallic derivatives of acetylacetone‡; and that in the enol a hydrogen ion may be similarly coordinated. Since the distinction between principal and subsidiary valencies cannot be maintained, the coordinated forms of the two enols would be identical.

This coordinated enol may be expected, like the sodium derivative, to persist in a polarized form, since it owes its very existence as a stable isomer to the possibility of forming by coordination a conjugated six-atom ring; but even this apparently obvious conclusion ought to be confirmed by experiment. The ketonic form, on the other hand, like maleic anhydride, contains only two unconjugated carbonyl-groups, and may easily revert to a non-polar form. Indeed, it is possible that di-ketones of this type give rise in general to one polarized and one unpolarized form, and that these are represented by a fully-polar coordinated enolic and a non-polar ketonic form respectively.

\* In the second formula the groups have been re-arranged so as to show the conjugated chain as the principal axis of the molecule.

† Trans. Chem. Soc. cxxiii. p. 2111 (1923).

‡ Morgan, Trans. Chem. Soc. cv. p. 193 (1914).

(b) *Coordination of Multipolar Ions.*—The importance of multipolar ions in the preparation of coordinated compounds has been pointed out in the Chemical Society paper already referred to\*, and has been discussed more fully in a series of articles in 'Chemistry and Industry.' It will therefore suffice here to direct attention to the fact that we have already succeeded in preparing in this laboratory coordinated-derivatives of compounds which have been studied hitherto as examples of dynamic isomerism, and that the liaison between these two lines of investigation has provided another very fertile field of research.

### 8. *Summary.*

(a) The theory of intramolecular ionization can be extended to organic compounds if it be assumed that double bonds can assume a form in which one carbon atom carries *eight* L-electrons, but the other only *six*, one pair of electrons only being shared. Since the former atom is then negatively and the latter positively charged, this type of double bond may be represented as made up of one covalency and one electrovalency.

(b) This extension of the theory of intramolecular ionization brings the reactivity of organic compounds into line with the well-recognized activity of inorganic ions, and makes it possible to regard all chemical action as ultimately ionic in character.

(c) The resting forms of the molecules need not be identical with their ionized or reactive forms. Examples are given, however, of organic compounds which probably have a permanently ionized structure, comparable with that of metallic salts. In other cases evidence is quoted to show that this condition results from a definite process of activation.

(d) Attention is directed to several phenomena which receive a simple explanation in the "crossed polarities" of compounds which have hitherto been classed as "conjugated."

(e) The properties of "multipolar ions" are referred to as furnishing a basis for a novel theory of tautomeric ions, and an explanation of their readiness to yield coordination-compounds.

University Chemical Laboratory,  
Cambridge.

\* Trans. Chem. Soc. cxxiii. p. 830 (1923).

CII. *On the Theory of Light-Quanta.* By H. BATEMAN, Professor of Mathematics, Theoretical Physics, and Aeronautics, California Institute of Technology, Pasadena \*.

IN a justly famous paper, in which he proposed his theory of the photoelectric effect, Einstein † showed that the idea of light-quanta is a plausible one when considered from the point of view of cavity radiation. For small densities of radiation of a definite frequency  $\nu$ , Wien's radiation formula may be regarded as applicable, and it appears that the radiation of this frequency behaves as if it consisted of discrete quanta, of energy  $h\nu$ , spatially independent of each other.

Einstein's analysis has been recently extended by Wolfke ‡, who shows that Planck's radiation formula can be interpreted to mean that cavity radiation consists of a series of partial radiations thermodynamically independent of each other, the constituents of each order being distributed as regards frequency according to a law analogous to that of Wien. The density  $u$  of radiation whose frequency lies between  $\nu$  and  $\nu + d\nu$  is in fact, by Planck's law,

$$u = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{\frac{h\nu}{kT}} - 1} = \sum_{s=1}^{\infty} u_s,$$

where

$$u_s = \frac{8\pi h\nu^3}{c^3} e^{-\frac{sh\nu}{kT}}$$

is the density of a partial radiation of order  $s$ .

By a repetition of Einstein's argument, in which use is made of the formula

$$S = - \frac{kE_s}{sh\nu} \left( \log \frac{e^{\frac{sh\nu}{kT}} E_s}{8\pi h\nu^3 V} - 1 \right),$$

for the entropy  $S$  of a partial radiation of order  $s$  and energy  $E_s = Vu_s$  contained in a volume  $V$ , Wolfke finds that the probability  $W_s$  that this energy may find itself at an arbitrary instant of time in the partial volume  $V'$  is

$$W_s = \left( \frac{V'}{V} \right)^{\frac{E_s}{sh\nu}},$$

\* Communicated by the Author.

† *Ann. der Phys.* xvii. p. 132 (1905).

‡ *Phys. Zeitschr.* xxii. p. 375 (1921).



and concludes that the  $s$ th partial radiation is composed of  $\frac{E_s}{sh\nu}$  spatially independent radiation quanta of energy  $sh\nu$ .

The analysis has recently been carried a step further by de Broglie \*, who points out that Einstein's formula

$$\bar{\epsilon}^2 = h\nu E + \frac{c^3 E^2}{8\pi\nu^2 V d\nu},$$

for the mean value of the square of the deviation  $\epsilon$  of the energy  $E$  (of radiation of frequencies  $\nu$  to  $d\nu$  contained in the volume  $V$ ) from its mean value  $E$ , can also be written in the form

$$\bar{\epsilon}^2 = \sum_{s=1}^{\infty} sh\nu E_s,$$

where  $E_s$  is the mean value of  $E_s$ . The term of order  $s$ , viz.  $sh\nu \bar{E}_s$ , is just the value one would expect if the energy  $E_s$  were made up of  $\frac{E_s}{sh\nu}$  light-quanta each of energy  $sh\nu$ .

The term  $\frac{c^3 E^2}{8\pi\nu^2 V d\nu}$  in Einstein's formula, which represents the mean value of  $\epsilon^2$  when use is made of the idea of interfering waves of all possible amplitudes and phases distributed in frequency according to the Rayleigh-Jeans law, can also be supposed to arise from the coherence of "light-atoms" of energy  $h\nu$  with the consequent formation of light-molecules, the energy of a "light-molecule" of order  $s$  being  $sh\nu$ . De Broglie concludes that if the quantum theory of light ever provides an interpretation of interference, it must introduce such "light-molecules."

In a later paper † de Broglie uses the methods of statistical mechanics to derive Wien's law of radiation from the hypothesis of discrete light-atoms. To obtain the correct numerical factor, he adopts Brillouin's suggestion that each light-atom is associated with an internal state of right- or left-handed circular polarization.

This indicates that a light-quantum may not be so essentially different from an electromagnetic field as some writers seem to expect. Indeed, if we imagine a light-quantum to be made up of superposed electromagnetic radiant fields of an elementary nature in which the light-vectors are transverse to the direction of motion of the quantum, the fact that

\* *Comptes Rendus*, clxxv. p. 811 (1922).

† *J. de Physique et le Radium*, iii. p. 422 (1922).

we can apparently add the energies of coherent light-quanta may mean that from a statistical point of view the directions of the light-vectors in the constituent fields are distributed at random or it may mean that the fields do not overlap.

Adopting a well-known argument due to the late Lord Rayleigh, let us consider  $n$  equal light-vectors transverse to the direction of propagation and subject to the usual vector law of addition. The magnitude of the resultant vector ranges from zero, when the vectors are parallel to the radii from the centre of a regular polygon to its corners, to a maximum value when all the vectors have the same direction. The mean value of the square of the resultant in a random distribution is, however,  $n$  times the square of the magnitude of one of the constituents, so that the energies appear to be additive.

The electromagnetic analogy is strengthened, too, by the successful development by Stark\*, Einstein†, and others‡ of the idea that a concentrated form of momentum of magnitude  $\frac{h\nu}{c}$  accompanies a light-quantum of energy  $h\nu$ , and has the same direction as the velocity of the quantum.

This relation between energy and linear momentum is a characteristic of all the forms of electromagnetic radiant fields that have been proposed as possible models of quanta.

From the point of view of the classical electromagnetic theory of Maxwell and Lorentz, a quantum consists of a radiant field of the ordinary type in which there is a concentration of energy in the initial stages of propagation, the distribution of energy becoming gradually more and more diffuse§.

In Sir Joseph Thomson's theory|| the concentrated energy is imagined to be located in or around discrete Faraday tubes, and light is supposed to consist of waves or kinks travelling along these tubes.

Sir W. H. Bragg¶ imagines that a form of electricity

\* *Phys. Zeitschr.* x. p. 902 (1909), xi. pp. 24, 179 (1910).

† *Ibid.* x. pp. 185, 817 (1909), xviii. p. 121 (1917); *Ver. d. D. Phys. Ges.* xviii. p. 318 (1916).

‡ R. Emden, *Phys. Zeitschr.* xxii. p. 513 (1921). A. H. Bucherer, *ibid.* xx. p. 451 (1920); *Ann. d. Phys.* lxxviii. pp. 1, 546 (1922). A. H. Compton, *Phys. Review*, May 1923; W. Duane, *Proc. Nat. Acad.* vol. ix. p. 158 (1923).

§ An attempt to account for a concentration of energy on the basis of the classical theory has been made by R. A. Houston, 'Nature,' April 24, 1919, p. 145.

|| 'Electricity and Matter.' London, 1904.

¶ *Phil. Mag.* xv. p. 663 (1908), xvi. p. 918 (1908), xx. p. 385 (1910).

travels with the waves and is responsible for the concentration of energy and momentum.

The original idea of the "neutral pair" of electric charges was that it consists of an electron neutralized by a positively-charged particle, such as a proton, but on account of the fact that, according to the usual ideas, electrons and protons cannot travel with the velocity of light, it seems better to regard any electric charges that travel with waves of light as consisting of an entirely different form of electricity which can travel with the velocity of light and still be associated with finite amounts of energy and momentum. There is nothing unreasonable in this supposition, for the laws which determine the structures of the electron and proton may quite likely determine also a third form which can travel with the velocity of light and have either a positive or negative charge\*.

The type of electricity we have in mind is not essentially different from the "æther" particles which are the carriers of electromagnetic fields of the ordinary type. The difference is simply one of degree, as we shall endeavour to show later on. Indeed, it is possible to adopt the view that the electric charges travelling with the waves are only convenient mathematical symbols for something which is quite compatible with the classical electromagnetic wave theory, the electric charges appearing only when a limiting process is carried out. There is some doubt as to whether this view is quite sound, but the point at issue will be brought out in the discussion.

Sir William Bragg has put forward an argument† in favour of the idea of the existence of actual electric charges in the waves which has never been satisfactorily answered. "The corpuscular form of the X- and  $\gamma$ -ray, and its energy relations to the  $\beta$ -ray which is its origin, and the  $\beta$ -ray which is its conclusion are the principal things which any theory must account for, and any model must illustrate. For this reason the spreading pulse of Stokes fails; and so does the kink in the tube of force of J. J. Thomson. The former diffuses its energy over a broadening surface, the latter over a lengthening line."

It is true that the rate at which the line lengthens may be very slow if the velocity of oscillation at the source of light is always very small, and the shape of a line of force is

\* This is true, for instance, in the case of one law consistent with the theory of relativity and capable of furnishing discrete charges in uniform motion. *Phys. Review*, xx. p. 243 (1922); 'Nature,' April 28, 1923.

† British Association Report, 1911, p. 340.

determined by the classical theory \*, but the author does not feel that this argument is quite sufficient to meet Bragg's objection. The objection fails, however, if we depart slightly from the classical theory and assume that a line of force (or, rather, a line round which radiant energy is concentrated) is generated by light-particles which are projected in a constant direction from the different positions of an oscillating charge. When such a theory of discrete Faraday tubes is adopted, it seems necessary to suppose that a form of electricity is radiated from an accelerated charge, for a continuous field in which the lines of force have the desired form is specified by equations of type †

$$H_x = \frac{\partial(\omega, \tau)}{\partial(y, z)}, \quad E_x = \frac{1}{c} \frac{\partial(\omega, \tau)}{\partial(x, t)}, \quad . \quad . \quad . \quad (1)$$

where

$$[x - \xi(\tau)]^2 + [y - \eta(\tau)]^2 + [z - \zeta(\tau)]^2 = c^2(t - \tau)^2$$

and

$$\omega = \frac{e}{4\pi} \frac{c^2 - \xi'^2 - \eta'^2 - \zeta'^2}{c^2(t - \tau) - (x - \xi)\xi' - (y - \eta)\eta' - (z - \zeta)\zeta'},$$

the primes denoting differentiations with respect to  $\tau$ . In this field, electricity is radiated from the moving singularity  $[\xi(\tau) \cdot \eta(\tau) \cdot \zeta(\tau)]$  with the velocity of light, and can be regarded as made up of electric dipoles.

When Poynting's vector is supposed to determine the flow of energy, it appears that there is no flow of energy to infinity in this continuous field even when the moving singularity has an accelerated motion. The field may thus furnish us with a crude model of the field of an electron describing a non-radiating orbit round a positive nucleus, but the model is probably not correct, because it is unlikely that the electric dipoles would move *freely* in the field of the positive nucleus. The field may still be of some service in predicting the behaviour of an atom under the influence of an external field, as will be seen later in a brief discussion of Prof. Whittaker's quantum mechanism in the atom.

If the theory of discrete Faraday tubes is developed somewhat in the manner suggested, it is not essentially different from that form of electromagnetic theory in which a concentration of radiant energy is associated with the presence of a form of electricity travelling with the waves. This form of electromagnetic theory may be regarded as due in the first

\* Bull. Amer. Math. Soc. xxvii. p. 217 (1921).

† Proc. London Math. Soc. xviii. p. 95 (1919); Phil. Mag. xli. p. 107 (1921).

place to Sir W. H. Bragg, Oliver Heaviside\*, and Levi Civita†.

A type of electromagnetic field which furnishes a simple working model of radiation with a concentration of energy may be specified by vectors  $\mathbf{E}$  and  $\mathbf{H}$  with components

$$\left. \begin{aligned} E_x = H_x = 0, \quad E_y = H_y = \frac{\partial \Omega}{\partial y} f\left(t - \frac{x}{c}\right), \\ E_z = -H_z = \frac{\partial \Omega}{\partial z} f\left(t - \frac{x}{c}\right), \end{aligned} \right\} \quad (2)$$

where  $\Omega$  is a function of  $y$  and  $z$  whose derivatives are large near some point or points of the  $yz$ -plane and small elsewhere.  $\Omega$  may even be zero in certain parts of the plane.

This radiation possesses many of the familiar properties of plane waves of light; thus  $\mathbf{E}$  and  $\mathbf{H}$  are perpendicular, equal in magnitude and transverse to the direction of propagation, but the direction of polarization generally varies over the wave-front.

Radiation of this type can, moreover, be obtained theoretically in a perfectly natural manner by the reflexion of "ordinary" plane waves of light at the surface of a mirror in the form of a paraboloid of revolution. This problem of reflexion will be treated here in an ideal fashion, for the paraboloid is supposed to extend to infinity and reflect perfectly; moreover, the amplitude of the incident waves is assumed constant over the wave-front, so that there is an infinite amount of energy in the incident waves. Reflexion at the paraboloid produces a concentration of an infinite amount of energy along the axis of the paraboloid and so a return radiation with a singular ray is to be expected.

To solve the problem, we represent the components of the electric force  $\mathbf{E}$  and magnetic force  $\mathbf{H}$  in the form

$$\left. \begin{aligned} H_x + iE_x &= f(\alpha, \beta) \frac{\partial(\alpha, \beta)}{\partial(y, z)} = \frac{i}{c} f(\alpha, \beta) \frac{\partial(\alpha, \beta)}{\partial(x, t)}, \\ H_y + iE_y &= f(\alpha, \beta) \frac{\partial(\alpha, \beta)}{\partial(z, x)} = \frac{i}{c} f(\alpha, \beta) \frac{\partial(\alpha, \beta)}{\partial(y, t)}, \\ H_z + iE_z &= f(\alpha, \beta) \frac{\partial(\alpha, \beta)}{\partial(x, y)} = \frac{i}{c} f(\alpha, \beta) \frac{\partial(\alpha, \beta)}{\partial(z, t)}, \end{aligned} \right\} \quad (3)$$

where  $i = \sqrt{-1}$ .

\* 'Electromagnetic Theory,' vol. iii. p. 477 (1922); 'The Electrician,' Nov. 29, 1901.

† *Comptes Rendus*, cxlv. p. 417 (1907); *Rend. Lincei*, xviii. p. 83 (1909). The theory has been developed by the author in a number of papers. See, for instance, *Phil. Mag.* xxvi. p. 579 (1913); *Proc. London Math. Soc.* xviii. p. 95 (1919), xxi. p. 256 (1921).

Let the equation of the paraboloid be  $r+x=a$ , the origin being at the focus and  $r$  being the distance from the origin.

For the incident wave we write

$$\alpha = y - iz, \quad \beta = t - \frac{r}{c}, \quad f(\alpha, \beta) = F(\beta),$$

where  $F(\beta)$  is real, the light being linearly polarized.

The reflected wave may be derived by means of the transformation \*

$$x' = a - r, \quad t' = t, \quad y' = \frac{ay}{r+x}, \quad z' = \frac{az}{r+x},$$

which leaves points on the surface of the paraboloid unchanged. For this wave

$$\alpha = a \frac{y - iz}{r+x}, \quad \beta = t - \frac{a-r}{c}, \quad f(\alpha, \beta) = -F(\beta),$$

and it is easily seen that there is a singular ray  $r+x=0$  for which  $E$  and  $H$  are infinite.

After passing through the focus this wave is presumably represented by

$$\alpha = a \frac{y - iz}{x-r}, \quad \beta = t - \frac{a+r}{c}, \quad f(\alpha, \beta) = +F(\beta),$$

and on a second reflexion at the surface of the paraboloid we obtain a plane wave represented by

$$\alpha = -\frac{a^2}{y+iz}, \quad \beta = t + \frac{x-2a}{c}, \quad f(\alpha, \beta) = -F(\beta).$$

This return wave has the axis of  $x$  as a singular ray, and electric dipoles, whose particular orientation in a transverse direction depends on the nature of the polarization, may be supposed to travel along the axis of  $x$ . We have, in fact,

$$E_x = 0, \quad E_y = \frac{a^2}{c} F(\beta) \frac{z^2 - y^2}{(y^2 + z^2)^2}, \quad E_z = -\frac{a^2}{c} F(\beta) \frac{2yz}{(y^2 + z^2)^2},$$

$$H_x = 0, \quad H_y = +E_z, \quad H_z = -E_y;$$

and it is seen that the lines of electric force in the plane of  $yz$  are those of an electric dipole at the origin whose axis is in the direction of the axis of  $y$  when  $F(\beta)$  is negative. At a point on the axis of  $z$  close to the origin the direction of

\* Proc. London Math. Soc. viii. p. 487 (1910).

the electric force is opposite to that of the polarization associated with the dipole.

By simply concentrating an electromagnetic field of a familiar type, we can in the limit, so to speak, create a type of electric dipole which travels with the velocity of light. It is true that the effect of diffraction has been eliminated by making the paraboloid extend to infinity, and it may be argued that with a paraboloid of finite size the true reflected wave would differ somewhat from the type imagined here in having no infinitely great concentration of energy; but as the paraboloid gets larger and larger, the effect of the diffracted light will presumably become small and the reflected wave tend more and more to the above type. There is still some uncertainty, however, regarding the correctness of this limiting solution from a physical standpoint, because we have four superposed fields some of which may exert forces on the moving electric dipoles associated with the others and produce some change. If this is the case, some type of field must be associated with the changes produced in the strength and motion of the electric dipoles, and our solution of the problem is incomplete. An interesting point arises here when we consider the state of affairs just before the passage to the limit. To obtain the limiting solution in which the moving electric dipoles are modified by the superposed fields, it seems necessary to assume that some change occurs when two electromagnetic fields of the ordinary type are superposed, and though generally negligibly small, it becomes quite marked when there is a concentration of energy in one or both of the fields.

This leads us to the conclusion that in general a secondary field is produced when the electromagnetic fields are superposed, and this may be the reason for the apparent failure of the classical theory to account for the properties of Bohr's hydrogen atom. The electron moves in the intense field of the nucleus, and no doubt a secondary field is produced when the fields of the electron and nucleus are superposed.

The existence of a secondary field may be necessary to maintain Newton's third law of motion. In the classical theory it is generally assumed that a field which accelerates an electron or proton is not directly modified although some change is produced in the field of the accelerated charge. It seems more natural to assume that the accelerating field receives a back kick and is in some way modified. Indeed, in Einstein's theory of light-quanta an atom is supposed to recoil when it emits a light-quantum in one direction, and is supposed to receive a kick when it absorbs a light-quantum.

There is one case in which no secondary field may be produced when two fields are superposed, and this is when the invariants  $E^2 - H^2$  and  $(EH)$  for the total field are the sums of the corresponding invariants for the individual fields\*. This is the case, for instance, when two fields of type (2) with different functions  $f$  and  $\Omega$  are superposed, and it should be noticed that each field exerts no force on the electric charges associated with the other. The electric charges, in fact, move freely under no forces, and no forces are needed to keep them intact.

To obtain a radiant field with a finite amount of energy in a concentrated form, we may superpose a number of fields of type (2) so as to obtain something like a continuous volume distribution of electricity, or we may adopt some method of averaging similar to that adopted by Lorentz in his theory of a dielectric.

If the first method be adopted we still have expressions of type (2), but there is a volume density of electricity,

$$\rho = f\left(t - \frac{x}{c}\right) \left[ \frac{\partial^2 \Omega}{\partial y^2} + \frac{\partial^2 \Omega}{\partial z^2} \right],$$

which moves in the direction of the axis of  $x$  with the velocity of light. The total energy is then finite if the integrals

$$\iint \left[ \left( \frac{\partial \Omega}{\partial y} \right)^2 + \left( \frac{\partial \Omega}{\partial z} \right)^2 \right] dy dz = W$$

and

$$\int_{-\infty}^{\infty} \left[ f\left(t - \frac{x}{c}\right) \right]^2 dx = I$$

are both finite. If, in particular †, we have

$$f\left(t - \frac{x}{c}\right) = \frac{\sin 2\pi\nu\left(t - \frac{x}{c}\right)}{t - \frac{x}{c}} = \int_0^{2\pi\nu} \cos p\left(t - \frac{x}{c}\right) dp,$$

the value of  $I$  is  $2\pi^2\nu c$  and is proportional to  $\nu$ .

\* This criterion is suggested simply by the example and its invariance under a relativity transformation. It should, perhaps, be replaced by some other criterion, such as the additiveness of  $E^2 - H^2$  alone or the absence of forces exerted by each individual field on the charges associated with the other.

† If this form of function does actually occur in the mathematical representation of a quantum, it seems to suggest that in the emission of a quantum an electron begins by performing small oscillations of frequency  $\nu$  about the initial orbit. The oscillations get larger and larger, and finally die down when the electron reaches a state in which it is performing small oscillations of frequency  $\nu$  about the final orbit.



A similar value is obtained by writing

$$r\left(t - \frac{x}{c}\right) = -\frac{1 - \cos 2\pi\nu\left(t - \frac{x}{c}\right)}{t - \frac{x}{c}} = \int_0^{2\pi\nu} \sin p\left(t - \frac{x}{c}\right) dp.$$

In both cases there is a concentration of energy, and if  $W$  is regarded as a universal constant the total energy is proportional to  $\nu$ , and we obtain a simple model of a light-quantum. To obtain a model of a quantum with circular polarization it is necessary to superpose two fields in which the dipoles are perpendicular, one field being of the first type and the other of the second type. The resulting field is then specified by vectors of type

$$H_x + iE_x = 0,$$

$$H_y + iE_y = i(H_z + iE_z) = \phi(y - iz) \int_0^{2\pi\nu} e^{\pm ip\left(t - \frac{x}{c}\right)} dp,$$

the  $+$  sign referring to left-handed circular polarization and the  $-$  sign to right-handed circular polarization.

An interesting point arises when an attempt is made to represent a linearly-polarized quantum for a limited portion of the wave-front by field components of type

$$E_x = H_x = E_y = H_y = 0, \quad E_y = H_z = A \frac{\sin 2\pi\nu\left(t - \frac{x}{c}\right)}{t - \frac{x}{c}}$$

where  $A$  is constant.

If such a quantum could pass without change of form through the electrostatic field of a condenser, say

$$E_x = E_z = 0, \quad E_y = E',$$

the total flow of energy across an area perpendicular to the axis of  $x$  would presumably be represented by

$$c \int_{-\infty}^{\infty} \left[ A^2 \frac{\sin^2 2\pi\nu\left(t - \frac{x}{c}\right)}{\left(t - \frac{x}{c}\right)^2} + AE' \frac{\sin 2\pi\nu\left(t - \frac{x}{c}\right)}{t - \frac{x}{c}} \right] dt \\ = 2\pi^2\nu c A^2 + \pi c AE',$$

and is thus increased or decreased by the presence of the electrostatic field. It seems unlikely that this would actually occur, and it is more probable that the quantum is modified

in some way by the electrostatic field. In any case the effect of the field depends on the sign of  $A$ , and so is different for quanta of opposite phase. The effect may not occur in the case of radiations in which the time factor has an average value zero, and is, for instance,

$$\sin 2\pi\nu\left(t - \frac{x}{c}\right), \quad \cos 2\pi\nu\left(t - \frac{x}{c}\right), \quad \text{or} \quad \frac{1 - \cos 2\pi\nu\left(t - \frac{x}{c}\right)}{t - \frac{x}{c}},$$

the integration extending in the last case for a complete number of periods on each side of  $t = \frac{x}{c}$ .

If the method of averaging be adopted, it seems reasonable to specify the resultant field by means of an electric force  $E$ , an electric displacement  $D$ , a magnetic force  $H$ , and a magnet induction  $B$ , and to write \*

$$\begin{aligned} E_x &= 0, & E_y &= \frac{\partial \Omega}{\partial y} f\left(t - \frac{x}{c}\right), & E_z &= \frac{\partial \Omega}{\partial z} f\left(t - \frac{x}{c}\right), \\ B_x &= 0, & B_y &= -\frac{\partial \Omega}{\partial z} f\left(t - \frac{x}{c}\right), & B_z &= \frac{\partial \Omega}{\partial y} f\left(t - \frac{x}{c}\right), \\ D_x &= 0, & D_y &= \frac{\partial \Gamma}{\partial z} f\left(t - \frac{x}{c}\right), & D_z &= -\frac{\partial \Gamma}{\partial y} f\left(t - \frac{x}{c}\right), \\ H_x &= 0, & H_y &= \frac{\partial \Gamma}{\partial y} f\left(t - \frac{x}{c}\right), & H_z &= \frac{\partial \Gamma}{\partial z} f\left(t - \frac{x}{c}\right), \end{aligned}$$

where  $\Omega$  and  $\Gamma$  are functions of  $y$  and  $z$ . The equations

$$\text{curl } H = \frac{1}{c} \frac{\partial D}{\partial t}, \quad \text{div. } D = 0,$$

$$\text{curl } E = -\frac{1}{c} \frac{\partial B}{\partial t}, \quad \text{div. } B = 0$$

are then satisfied. If, moreover, the energy density is given by

$$\frac{1}{2}(ED) + \frac{1}{2}(BH) = \frac{\partial(\Omega, \Gamma)}{\partial(y, z)} \left[ f\left(t - \frac{x}{c}\right) \right]^2,$$

and the flow of energy by

$$c(E_y H_z - E_z H_y) = c \frac{\partial(\Omega, \Gamma)}{\partial(y, z)} \left[ f\left(t - \frac{x}{c}\right) \right]^2 = c(D_y B_z - D_z B_y),$$

\* This type of field may be generalized by using expressions of type (3) for the components of  $H + iE$  and similar expressions with a different  $a$  and  $f$  for the components of  $B + iD$ . In these expressions,  $\beta$  is the phase parameter and  $f$  need no longer be considered as a function of  $a$  and  $\beta$ , if there is a volume distribution of electricity.

energy and momentum again flow with the velocity of light, and a special form may be given to  $f$ , as before, to obtain a concentration of energy. The corresponding form of  $W$  is now

$$\iint \partial(\Omega, \Gamma) dy dz = \iint d\Omega d\Gamma.$$

It is probable that the proposed expressions give us models of only some of the simplest forms of quanta, because when a quantum of one of these types is reflected obliquely at a moving mirror, a quantum radiation of another type is obtained.

If we use a field of type (3) to form a simple model of a quantum radiation, reflexion at a moving mirror is easily studied by means of a space-time transformation.

When the equation of the mirror is  $x=ut$ , an appropriate transformation is †

$$x^* = x - \frac{2c^2}{c^2 - u^2}(x - ut), \quad y^* = y;$$

$$t^* = t - \frac{2u}{c^2 - u^2}(x - ut), \quad z^* = z;$$

and we may put

$$\alpha^* = \alpha, \quad \beta^* = \beta, \quad f^*(\alpha^*, \beta^*) = -f(\alpha, \beta).$$

There is, however, some uncertainty as to the correctness of this analysis, because there may be an interaction between the incident and reflected field with the formation of a secondary field. The analysis may, however, be supposed to give us a first approximation.

When the incident field is of type (2), we have

$$\alpha = \Omega(y, z) + i\Lambda(y, z), \quad \beta = ct - x, \quad f(\alpha, \beta) = f\left(t - \frac{x}{c}\right),$$

$$\alpha^* = \alpha, \quad \beta^* = \frac{(t^* + x^*)(c + u)}{c - u}.$$

$$\text{Hence, if} \quad f\left(t - \frac{x}{c}\right) = \frac{\sin 2\pi\nu\left(t - \frac{x}{c}\right)}{t - \frac{x}{c}},$$

the reflected field is of the same type, but its frequency is

$$\nu^* = \nu \frac{c + u}{c - u},$$

† Phil. Mag. xviii. p. 894 (1909). xix. (May 1910). Bull. Nat. Research Council, vol. iv. no. 24. p. 109 (1922).

in accordance with Doppler's principle. It is quite possible, of course, that when the incidence is oblique, the secondary field is of such a nature that effectively the reflected quantum radiation is still of the simple type (2). This question of the interaction between fields is a difficult one; some light may be shed upon it, however, by the recent researches of A. H. Compton and W. Duane.

A slight indication of the nature of the interaction may, perhaps, be obtained by a slight modification of Whittaker's quantum mechanism in the atom.

An essential feature of Whittaker's quantum mechanism is that something analogous to a magnetic current or an electric shell is induced by the magnetic field of an approaching electron.

The secondary field of an electron and a proton may provide such a mechanism, especially if it contains entities analogous to electric dipoles travelling with the velocity of light; for these may be orientated under the action of the magnetic field, so that they tend to set themselves more nearly parallel to the electron's line of motion, and thus produce a force retarding the electron\*.

The dipoles in the secondary field may be regarded as analogous to eddies. This analogy may, perhaps, be made a little clearer by considering the diffraction of light by a black screen, on the supposition that a type of radiation from the edge of the screen is superposed upon the direct light or darkness obtained by the methods of geometrical optics. This supposition is in some respects analogous to the hypothesis of inflected rays adopted by Young in his Theory of Diffraction†, but the radiation issuing from the edge of the screen seems to be composed of elementary radiations with singular rays consisting of entities analogous to electric dipoles moving along straight lines with the velocity of light. There is an elementary radiation of this type for each element of the edge, and the infinite values of the light-vectors disappear on integration, leaving only finite discontinuities just sufficient to balance those introduced by the methods of geometrical optics. The solution of the mathematical problem has been discussed in detail by F. Kottler‡,

\* If the atomic electron's field is regarded to a first approximation as of type (1), the dipoles radiated in the plane of the electron's orbit will initially have their axes in this plane. The field of the approaching electron will tend to swing them out of this plane.

† See R. W. Wood's 'Physical Optics,' p. 183.

‡ *Wiener Berichte*, cxxix. p. 1 (1920); *Ann. d. Phys.* lxx. p. 405 (1923). The method was proposed also by the author, and illustrated by an example taken from the theory of sound: 'Electrical and Optical Wave Motion,' Ch. V.

who regards it as an indication that radiation with a concentration of energy has a physical existence. Kottler illustrates the theory by a simple example based on Kirchhoff's treatment of diffraction which he regards as quite rigorous in the case of a black screen.

Treating the light as unpolarized, he specifies it by a scalar quantity  $Aue^{ikt}$ , where  $A$  and  $k$  are constants. For the incident light  $u = u_0 = \frac{1}{r} e^{-ikr}$ , where  $r$  is the distance from the source. For the total light Kirchhoff's formula gives

$$\begin{aligned} u &= u_0 + \frac{1}{4\pi} \int dS \left[ u_0 \frac{\partial}{\partial n} \left( \frac{1}{R} e^{-ikR} \right) - \frac{\partial u_0}{\partial n} \frac{1}{R} e^{-ikR} \right] \\ &= u_0 + \frac{1}{4\pi} \int dS \operatorname{rot}_n \left\{ \frac{1}{rR} e^{-ik(r+R)} \frac{[rR]}{rR + (rR)} \right\}, \end{aligned}$$

where the integration extends over the illuminated part of the screen and the suffix  $n$  denotes that we must take the component of  $\operatorname{rot} \{ \}$  along the outward normal to the surface. The vectors  $r$  and  $R$  are drawn radially from the source, and  $P$  to a point on the black surface.

Kottler transforms the integral into a line integral round the boundary of the illuminated portion of the screen (*i. e.*, the edge when the screen has a sharp edge). In applying Stokes's theorem a separate treatment must be given of the case in which the line joining  $P$  to the source meets the illuminated portion of the screen. In this case it is convenient to use the equivalent formula

$$\begin{aligned} u &= -\frac{1}{4\pi} \int dS \left[ u_0 \frac{\partial}{\partial n} \left( \frac{1}{R} e^{-ikR} \right) - \frac{\partial u_0}{\partial n} \frac{1}{R} e^{-ikR} \right] \\ &= -\frac{1}{4\pi} \int dS \operatorname{rot}_n \left\{ \frac{1}{rR} e^{-ik(r+R)} \frac{[rR]}{rR + (rR)} \right\}, \end{aligned}$$

taken over a surface which has the same boundary as the illuminated portion of the screen, and together with it forms a complete barrier to the incident light. Kottler finds that in both cases \*

$$u = \{u_0\} + \frac{1}{4\pi} \int [rR]_s ds \frac{e^{-ik(r+R)}}{rR + (rR)},$$

where  $[rR]_s$  denotes the component of the vector product  $[rR]$  in the direction of the line element  $ds$ . The term  $\{u_0\}$

\* See also G. A. Maggi, *Ann. di. Mat.* xvi. p. 37 (1888). The transformation indicates the relation between the ideas of Young and Fresnel.

represents light obtained by the methods of geometrical optics, and is thus zero inside the geometrical shadow and equal to  $u_0$  outside. The light diffracted from the edge of the screen has singular rays because the integrand becomes infinite when the line joining the source to P meets the edge of the screen before it reaches P.

The analogy between diffraction by a black screen and the flow of a fluid round an obstacle may be quite close. In the hydrodynamical problem a first approximation to the solution is obtained by using the method of discontinuous flow, and the surface of discontinuity may be regarded as analogous to the boundary of the geometrical shadow. To obtain a second approximation we must regard the surface of discontinuity as surrounded by a region of eddy motion, and the optical analogue of the eddy seems to be the electric dipole.

It is rather significant that the singular rays appear when the diffraction problem is solved by means of a simple integral instead of a double integral. This may be compared with the fact that in addition to the very general solution of the wave-equation expressed by Whittaker and Watson in the form of a double integral

$$V = \int_0^\pi \int_0^{2\pi} F(x \sin \alpha \cos \beta + y \sin \alpha \sin \beta + z \cos \alpha - ct, \alpha, \beta) d\alpha d\beta$$

there is also a very general solution in the form of a simple integral \*

$$V = \int_0^{2\pi} f(x \cos \theta + y \sin \theta - ct, x \sin \theta - y \cos \theta - iz, \theta) d\theta,$$

in which each element of the integral generally represents a wave-function with singular rays. The transition from one form to the other can, no doubt, be made in many ways. One transformation is provided by the integral formula

$$e^{ik(x \sin \alpha \cos \beta + y \sin \alpha \sin \beta + z \cos \alpha - ct)} = \frac{1}{2\pi} \int_0^{2\pi} \frac{e^{ik[x \cos \theta + y \sin \theta - ct + i \cos \alpha (x \sin \theta - y \cos \theta - iz)]}}{1 - \tan \frac{\alpha}{2} \cdot e^{i(\beta - \theta)}} d\theta,$$

which is easily proved with the aid of Cauchy's theorem. In this case the singular rays are at infinity, and the wave-function represented by the integral has no discontinuities in finite regions of space.

\* This is only one of a large class of definite integral solutions obtained by generalizing fields of type (3). See Bull. National Research Council, iv. no. 24, p. 144 (1922).

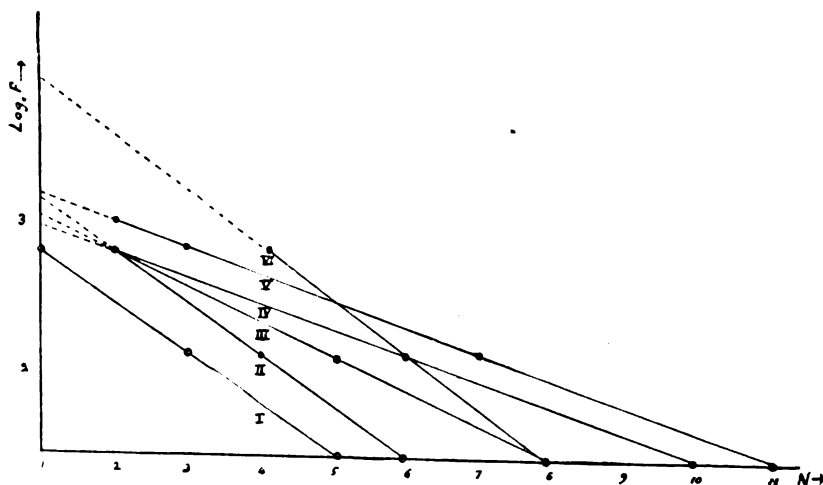
CIII. *Some further Observations on the Relation between the Focal Length of Microscope Objectives and the Number of Fringes seen in Convergent Polarized Light.* By F. IAN G. RAWLINS\*.

THE object of the present paper is to describe a further series of experiments on the relationship which exists between the number of interference rings which are seen in crystal sections (cut in various directions) in convergent polarized light by means of a microscope.

The first series of readings already described by the author† referred only to crystalline plates cut perpendicularly to the optic axis in the case of uni-axial crystals, and perpendicularly to the acute bisectrix for bi-axial crystals.

In the case now under consideration, however, sections cut at various orientations were investigated, and in every instance, as shown by the graph, the equation  $F = F_0 e^{-AN}$  is satisfied.

Fig. 1.



$F$  is the focal length of the objectives in millimetres,  $N$  is the number of rings observed, while  $A$  is a parameter which is easily seen to be given by the expression  $A = \frac{d \log_e F}{dN}$ .

The numerical values of  $A$  are given in the table, together with the experimental data and the orientations.

\* Communicated by the Author.

† Phil. Mag. xliii. p. 766 (April 1922).

The apparatus was substantially the same as that already described \*, except that the Wratten filter was abolished and the observations made by sodium light. The same sub-stage, condenser, tube-length, eyepiece, and Becké lens have been used throughout.

Considerable interest centres round the physical significance of the constant A. It will be noticed from the graph how there is a tendency for the lines representing the family  $\log_e F = \log_e F_0 - AN$  to fall into parallel groups. Thus the curves I, II, and VI are parallel, as are also IV and V. Experiments are contemplated to investigate this more closely, the results of which it is hoped may be communicated later. Meanwhile, the validity of the original exponential expression is considerably extended.

Number on graph.	I	II	III	IV	V	VI
Mineral .....	Tourmaline.	Quartz.	Barytes.	Barytes.	Topaz.	Topaz.
Orientation .....	optic axis.	optic axis.	⊥ one optic axis.	⊥ obtuse bisectrix.	⊥ one optic axis.	one optic axis.
Thickness in mm.	1.60	2.00	2.40	3.00	1.35	0.50
$A = \tan \alpha \frac{d \log_e F}{dN}$	.1853	.3640	.2217	.3640	.1853	.3640
Objective's focal length = F mm.	Number of Rings N.					
4	5	6	8	10	11	8
8	3	4	5	6	7	6
16	1	2	2	2	3	4
22	...	..	..	...	2	...

In conclusion, the author wishes to express his obligations to Mr. C. W. Hawksley for his help with the apparatus, and also to Mr. G. W. Brown for his skill in the preparation of material.

\* *Loc. cit.*



CIV. *The Emission of Secondary Electrons from Metals under Electronic Bombardment.*

*To the Editors of the Philosophical Magazine.*

GENTLEMEN,—

**I**N the *Philosophical Magazine* for May 1923, I gave an account of the secondary emission obtained from the nickel plate of a three-electrode valve, and criticized some conclusions arrived at by Prof. Horton and Dr. Davies in somewhat similar investigations.

In the experiments on secondary emission the electrons from a hot filament in a gas-free valve move towards a grid whose potential is  $V_G$  above the filament, and a proportion of the electrons pass through the grid and strike the plate whose potential is  $V_P$  above the filament.

The plate current was measured for various values of the potential  $V_P$ ,  $V_G$  being kept constant, and the curves obtained are reproduced here in figs. 1 and 2.

The main feature of the curves is the fact that over a considerable range of values of  $V_P$  the current decreases as  $V_P$  increases, which is of course due to secondary emission. The details of the curves however, such as the points at which the plate current attains its maxima and minimum values, appear to me to depend on the grid; but Prof. Horton and Dr. Davies in a recent communication\* maintain that their results cannot be subject to variations depending on the grid, as they used a grid of very fine mesh.

The use of grids is now very common, particularly in work on ionizing and radiating potentials, and it seems therefore worth while to discuss more fully how far the fineness of the grid can avoid the difficulties which I pointed out.

The peculiarity of the curves in fig. 1 is that, although the secondary emission or reflexion depend upon the velocity of impact on the plate, that is on  $V_P$  and not on  $V_G$ , the curves are entirely different for different values of  $V_G$ . It is not therefore possible to deduce directly from the shape of a curve accurate information about secondary emission, as there must be another factor which influences this shape.

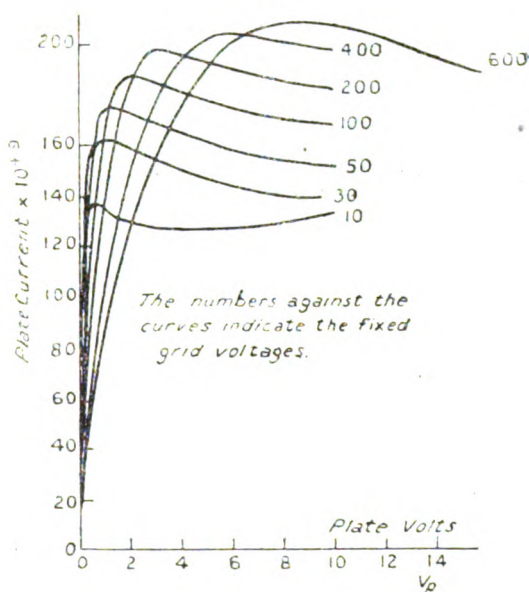
Prof. Horton and Dr. Davies used only one value of  $V_G$ , and deduced from a bend in their curve that secondary emission commenced for a velocity of impact corresponding to a potential drop of about 10 volts.

In my previous paper, I pointed out that the differences

\* *Phil. Mag.* July 1923, p. 129.

between the curves in fig. 1 were accounted for by the bending of the paths of the electrons which passed close to the grid wires. Bending occurs whatever the size of the grid wires and spaces, and the application of a magnetic field, which causes the electrons to move in spirals, will not eliminate its effects; and there is therefore no reason to suppose that, if Prof. Horton and Dr. Davies had used a different value of  $V_G$ , their bend would have occurred at the same place. They do not, however, appear to claim that their grid produced no deviation of the electrons, but they

Fig. 1.



still claim that the sharpness of the bend between the points F and G on their figure (Phil. Mag. July, p. 130, 1923) indicates the commencement of a new effect.

This bend occurs at the tenth point on their curve (counting from the left). A bend of equal sharpness is found at the twelfth point, but as they attributed no significance to the latter point, the writer assumed it could be accounted for by experimental error. An equal error of about 1.7 per cent. would, however, dispose of the sharpness of the bend at the tenth point on which their conclusions are based.

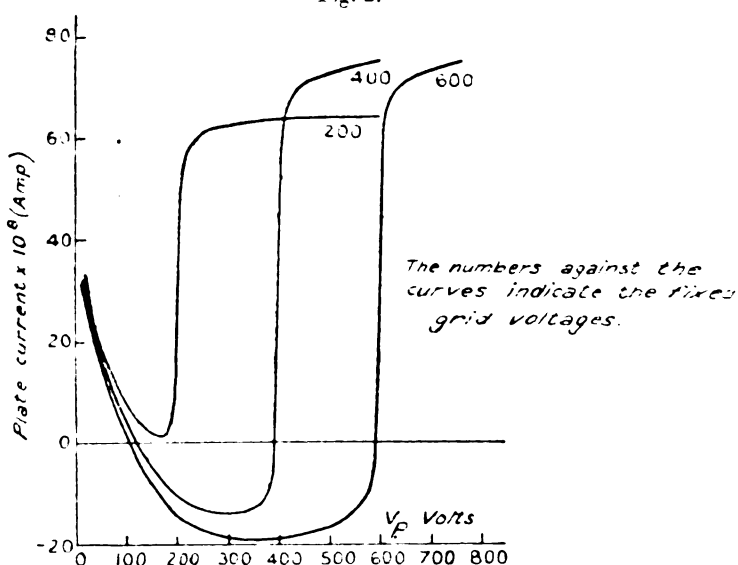
Those who are familiar with the use of the electrometer for the measurement of small currents and the difficulty of

keeping a steady, small emission from a filament, have reason to hesitate before accepting as evidence for important physical phenomena the result of experiments depending on the absence of an error of the order of 1.7 per cent.

The final rise of the curves (fig. 2) involves the question of how far the grid can be regarded as a shield.

This rise commences before  $V_P$  reaches the same value as  $V_G$ , and in this connexion the writer pointed out that the field near the plate actually did reverse before  $V_P$  reached the value  $V_G$ .

Fig. 2.



The writer is glad now that Prof. Horton and Dr. Davies have given the dimensions of their grid, to agree that in their experiments the electric force near the plate does not change sign until the grid is at nearly the same potential as the plate. But he cannot agree with them when they say that the phenomenon presents no difficulty of interpretation.

In their experiments secondary electrons begin to return to the plate when a field of about 5 volts is attracting them to the grid, which they attribute partly to a small voltage being necessary for saturation and partly to some of the secondary electrons being given off in holes of molecular dimensions in the plate.

An explanation involving this last assumption can scarcely be said to present no difficulty.

The plate current continues to increase as  $V_P$  is made larger than  $V_G$ , and Prof. Horton and Dr. Davies found that their current reached a saturation value when  $V_P - V_G = 9$  volts, interpreted as indicating that the maximum velocity of emission of the secondaries was equivalent to 9 volts. In my curves (fig. 2) I did not get a very definite saturation, and pointed out that the sharpness of the final bend was obscured owing to the fact that as  $V_P$  was increased, electrons which originally went direct to the grid from the filament were diverted to the plate.

Prof. Horton and Dr. Davies say on this point: "The proof that the shielding action of the grid was almost perfect disposes of Mr. Gill's contention that because no allowance was made for an increase with increasing plate potential of the primary current to the plate at the expense of the primary current to the grid the estimate of 9 volts. . . . is unreliable."

This statement involves a complete misapprehension of the effect of the grid. All that was shown by Dr. Appleton (to whom they refer) was that at the surface of the plate the shielding of their grid was nearly perfect. The question of whether an electron from the filament goes direct to the grid, or passes through it, has nothing whatever to do with the field at the surface of the plate, but is largely determined by the field in the neighbourhood of the grid wires.

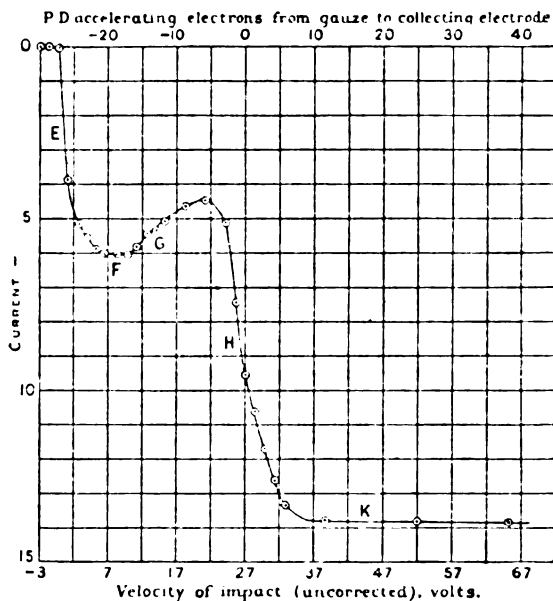
The phrase "shielding action of the grid" appears to be an unfortunate one, as implying that the field everywhere between the grid and the plate is determined solely by their potentials and not by that of the filament. What actually happens is that near the plate and up to a certain distance from the grid the field is determined very accurately by the potentials of grid and plate alone, and with the finer grid this is true over a larger space than with the more open type; but near the grid the field is influenced by the potential of the filament, and, as I pointed out in my original paper, the plane of the grid is not an equipotential surface. The potential at the centre of the grid spaces may, if the wires are thin, differ considerably from that of the grid wires owing to the large force just outside such a wire.

The above statement of Prof. Horton and Dr. Davies appears to imply that as the plate potential is increased, none of the primary current to the grid is diverted to the plate, since they say that my contention that this occurs is disposed of. This is equivalent to asserting that the number of electrons from the filament which passes through the grid

is constant so far as variation of the plate potential is concerned. If this supposition is taken as being correct and applied to their own curve, it leads to conclusions which are very difficult to accept.

Their curve (Phil. Mag. July, p. 130, 1923) (reproduced in fig. 3\*) shows that the total current passing through the grid is 13.8 units about, this being their measure of the plate current for  $V_p=36$  and upwards when no electrons return from the plate to the grid.

Fig 3.



For  $V_p=7$  the plate current is 6 units, and on the assumption that 13.8 units pass through the grid, since all of these reach the plate, the conclusion is that for 138 electrons hitting the plate 138-60 are returned to the grid by reflexion or secondary emission—*i. e.*, for a velocity of impact of only 7 volts we get a secondary emission and a reflexion of more than 50 per cent.

If the same reasoning be applied to the earlier portion of the curve, the result is still more surprising, and appears to indicate that as the velocity of impact is reduced *below* the equivalent of 7 volts the secondary emission (or reflexion) increases, while a consideration of the flat portion at F indicates that from 7 to 10 volts the secondary emission remains the same.

\* Their current ordinate is measured in the opposite direction to mine.

I do not think it can possibly be maintained that, if the field on one side of a grid is altered, the number of electrons which pass through will remain the same.

The chief conclusions about grids appear to be therefore:—

(1) It is difficult to find what proportion of the current from the filament passes through them.

(2) The electrons after passing through do not in general continue to move at right angles to the grid.

(3) The field between the grid and the next electrode is not everywhere independent of the potential of any other electrodes.

(4) The plane of the grid is not an equipotential surface, and the electrons passing through have different velocities.

The use of a very fine grid removes to some extent the difficulty (3), but does not necessarily get over the other three.

In addition, though this has not been discussed, there is sometimes the further complication of reflexion or secondary emission from the grid.

Yours faithfully,

E. W. B. GILL

Merton College,  
Oxford.

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CV. *On the Adiabatic and Isothermal Piezo-Electric Constants of Tourmaline.* By DAVID A. KEYS, M.A., Ph.D.\*

THE question of any large difference in the piezo-electric constant of tourmaline, when compressed adiabatically and isothermally, is one of the greatest importance in making measurements by the piezo-electric method †. In general, the crystal vessel is calibrated by applying static pressures to the crystals and finding the effect produced. The calibration pressures will necessarily be applied relatively slowly as compared with the time taken for the pressure in an explosive wave to reach its maximum. Thus the crystals are calibrated isothermally and used adiabatically. Any difference in the piezo-electric constant in the two cases will cause an error in calibration.

The experimental determination of the difference between

\* Communicated by the Author.

† Phil. Mag. vol. xlii. p. 473 (1921).

the adiabatic and isothermal effects is so difficult to carry out, that it seemed expedient to calculate thermodynamically the difference to be expected. This may be done as follows:—

Let one gram of the tourmaline be given a quantity of heat  $dQ$ . Then if  $T$  is the absolute temperature and  $dS$  the change in entropy, we have

$$\begin{aligned} dQ &= T \cdot dS \\ &= T \left( \frac{\partial S}{\partial T} \right)_P dT + T \left( \frac{\partial S}{\partial P} \right)_T dP \\ &= C_P dT - T \left( \frac{\partial v}{\partial T} \right)_P dP, \end{aligned}$$

because

$$\left( \frac{\partial S}{\partial T} \right)_P = \frac{C_P}{T}$$

and

$$\left( \frac{\partial S}{\partial P} \right)_T = - \left( \frac{\partial v}{\partial T} \right)_P.$$

In the case of solids,  $\frac{\partial v}{\partial T} = \alpha v_0$  where  $\alpha$  = coefficient of cubical expansion and  $v_0$  = volume of the gramme of tourmaline at  $0^\circ \text{C}$ .

Hence for an adiabatic change we have  $dQ=0$ , and therefore

$$C_P dT = T \left( \frac{\partial v}{\partial T} \right)_P dP = T \alpha v_0 dP$$

or

$$dT = \frac{T \alpha v_0}{C_P} \cdot dP.$$

Suppose the pressure suddenly increases by an amount  $P$  dynes. Then the consequent change in temperature will be

$$\Delta T = \frac{T \alpha v_0 P}{C_P} \dots \dots \dots (1)$$

Now, considering one gramme of tourmaline,  $v_0 = \frac{1}{d}$  where  $d$  = density of tourmaline at  $0^\circ \text{C}$ . Thus (1) becomes

$$\Delta T = \frac{T \alpha P}{C_P \cdot d} \dots \dots \dots (2)$$

When  $T = 17^{\circ} \text{C.} = 220^{\circ} \text{abs.},$

$$\alpha = 13.89 \times 10^{-6} \text{ }^{\circ},$$

$$d = 3.15 \text{ } \dagger,$$

$$C_p = 0.200 \text{ calories per gm.} = 0.84 \times 10^7 \text{ ergs per gm. } \ddagger ;$$

$$\therefore \Delta T = 1.52 \times 10^{-10} P \text{ in degrees centigrade.}$$

If  $P = 100 \text{ atmospheres} = 10^8 \text{ dynes, then}$

$$\Delta T = .0152^{\circ} \text{C.}$$

Owing to this change in temperature, we shall have a pyro-electric charge produced. The pyro-electric constant of tourmaline is 1.2 e.s. units per  $\text{cm.}^2$  per degree centigrade §. Hence the charge produced by this rise in temperature

$$= .018 \text{ e.s. units per cm.}^2$$

The piezo-electric charge produced by 100 atmospheres is

$$= 5.4 \times 10^{-8} \times 10^8 = 5.4 \text{ e.s. units per cm.}^2 \parallel$$

The resulting charge would be

$$= 5.4 - .018 = 5.382 \text{ e.s. units per cm.}^2$$

Hence the difference between the adiabatic and isothermal piezo-electric constants of tourmaline is only about 0.33 per cent. Consequently there is only a very slight error caused by calibrating the crystals isothermally and using them adiabatically.

Macdonald Physics Building,  
McGill University.

\* Voigt, *Kristallphysik*, p. 293.

† Landolt-Börnstein Tables.

‡ Abraham & Sacerdote, *Recueil de Constantes Physiques*, p. 311.

§ Poynting & Thomson, 'Electricity and Magnetism,' p. 153.

|| Poynting & Thomson, 'Electricity and Magnetism,' p. 160; also Curie, *Œuvres*, p. 23.



CVI. *Space.**By* NORMAN CAMPBELL, *Sc.D.*\**Summary.*

**I**T is inquired what is the connexion of the conception of "space" with the experimental geometry which was discussed in a previous paper. It is concluded that space, though based on the experimental concept "position," which is a typical pure derived magnitude, is itself a hypothetical idea and involved in theories rather than in laws. A brief and very summary outline of the theory of space, as it appears in classical physics, is given, and a few remarks offered on the alterations of this theory that are rendered necessary by the general theory of relativity.

1. In a previous paper† I discussed what laws were necessary in order that the three fundamental geometric magnitudes—length, angle, and area—should be measurable. It was concluded (1) that these magnitudes were similar to all other fundamental magnitudes in requiring for their measurement the laws of equality and addition; (2) that the conditions in which these laws are true are those which describe rigid bodies, and that, consequently, the only sound definition of a rigid body is one for which these laws are true; (3) that, from the fact that the laws are true and that these magnitudes are measurable, we can deduce a number of propositions, corresponding roughly to the contents of Books I., II., III., VI. of Euclid's Elements; (4) that the axioms on which those books are based correspond somewhat closely to statements of the necessary laws of measurement, and the proofs there given to those by which these propositions can be proved from these laws. The precise significance of the correspondence (4) will be estimated differently by different persons; the questions which it raises are personal and historical rather than scientific. But to me, at least, it seems sufficiently significant to justify the use of the term "geometry," or "experimental geometry," to describe the branch of physics which is concerned with the fundamental measurement of these magnitudes, and therefore with the properties common to all rigid bodies.

But geometry in this sense has nothing to do with space; and it is largely in order to draw attention to this fact that

\* Communicated by the Author.

† Phil. Mag. vol. xliv, p. 15 (1922).

I urge that the term is appropriate. For geometry is sometimes said to consist in the study of space; and here is a branch of science, at least closely allied to it, in which that conception finds no place whatever. The question therefore arises, what is the relation of the conception of space to experimental geometry? Is it a conception belonging to experimental science at all, or is it purely mathematical or philosophical? And, if it does belong to experimental science, is it a concept or a hypothetical idea \*? These are the questions which will be discussed in this paper.

2. Space is closely associated with position. Position takes its pre-scientific origin from relations instinctively recognized. The position of an object is connected, as Poincaré has pointed out, with the muscular movements necessary to bring it within the range of perception, visual or tactual. Two small objects, or points, have the same position if they are coincident, and therefore, by the meaning of coincidence, are attained by the same muscular movements. The identity of "visual" and "tactual" space arises from the important fact that points which are coincident for all observers, in respect of the movements that control visual perceptions, are also coincident in respect of those which control tactual perceptions.

Since they are based on primary sensations of the same kind, the crude conception of position and the crude conceptions of geometric magnitudes are closely connected. But it is important to insist that position, in its original meaning, is quite independent of the idea of a rigid body; objects have position even if they are not rigid bodies or parts of them; indeed, since one of the most important applications of the conception of position is to the interpretation of those changes which we call motion, and since such changes are inevitably associated with some absence of rigidity, it might be urged that the study of position and the study of rigid bodies were diametrically opposed. The close connexion between them in science arises only when an attempt is made to convert position from a crude to a scientific conception by measurement.

In order to measure position, we must find some method of assigning numerals to objects in such a way that identity of numerals denotes contiguity and diversity of numerals separation. Further, since we have some crude appreciation of magnitude of separation based on muscular sensation, it

\* These terms and many others employed here, such as derived and fundamental magnitude, numerical law, law of measurement, and so on, are used in the sense carefully defined in my 'Physics.'

is desirable that, in general, greater diversity of numerals shall correspond to greater separation. It is impossible to measure position as a fundamental magnitude (for two similar positions cannot be combined to give a third position different from either); it must be measured as derived, and the numerals to be assigned must be those denoting magnitudes of some other kind. The magnitudes that are used for this purpose are the geometric magnitudes which are characteristic of rigid bodies and were discussed in the preceding paper, *i. e.*, length, angle, and area. Probably these are the only magnitudes that can actually be used; but it must be noted that it is just conceivable that this limitation might not have existed. It is not impossible (to speak in terms of our present conceptions) that every point in space might have a different temperature; if that were so, position might be identified and measured by temperature. Or, if it is held that denotation by a single one-dimensional magnitude is inconsistent with a three-dimensional space, it might have been possible to use three magnitudes of different kinds, such as temperature, gravitational force, and electric potential. The association of the conception of position, and thence of space, with the geometric magnitudes may be an actual fact of the world as it exists, but it is not certainly inherent in the meaning of those conceptions. If there is any necessary association of space with the properties of rigid bodies, it arises rather from the fact that, when the most accurate measurements are to be made, points forming parts of the surface of rigid bodies are the only objects having position.

3. Position, then, is a derived magnitude measured by the fundamental geometric magnitudes, just as density (the magnitude connected with flotation) is measured by mass and volume, although, in its original meaning, it has nothing to do with those magnitudes. We proceed to ask what are the laws upon which this system of derived measurement depends.

Consider, first, the system in which position is fixed entirely by "distances." By the distance between two points we mean, in the first instance, the length of the straight line the ends of which are coincident with those points—that is a mere verbal definition. We take a number of points on the surface of some one rigid body and attempt to measure the position of other points from these points, which form the frame of reference. We immediately find that, whatever points of reference we choose, there are many points of which we want to measure the position, but which have no distance from some or all of the points of reference, because (owing

to the intervention of solid bodies, as we say now) we cannot place a straight line between the measured point and the points of reference. Measurement by any such system is made possible only by changing somewhat the meaning of distance. We permit the use of calipers, and propose to say that the distance of A from B is  $d$ , if two points on some rigid body can be brought into coincidence, first with A and B, and then with the ends of a straight line of length  $d$ . This change in the meaning of distance converts the conception into a definite concept, implying the truth of a law, namely that the distance determined by means of calipers is the same whatever the form of the calipers, so long as they are rigid. This is the first law involved in the measurement of position.

Having thus made possible the measurement of the distance between any point and the points of reference, we proceed to inquire whether the necessary condition can be fulfilled, that points are coincident and have the same position if, and only if, their distances from the points of reference are the same. It turns out that it is fulfilled if we choose at least four points of reference not lying in the same plane, and regard position as determined by the set of values of all these four or more distances. The second law of measurement is, therefore, that two points are coincident if, and only if, their distances from each of four or more non-coplanar points are the same. The third law, not of much importance for our present purpose, is that, if  $n$  points of reference are chosen, of which no four lie in a plane, there are  $n-3$  numerical laws relating the  $n$  distances of any point from the points of reference and the distances between those points.

The systems of "coordinates" more usually employed for fixing position, such as the Cartesian or the Eulerian, involve angles as well as distances. The nature of the calipers which such systems involve is much more complicated, but there is again a law corresponding to the first given above. To the second, of course, corresponds the law that three coordinates fix the point, while there is no law corresponding to the third; the coordinates are independent. The recognition of alternative systems of coordinates and of measuring position requires the knowledge of further laws describing their equivalence; if the position of a point measured with one system of coordinates relative to one frame of reference is known, numerical laws must be available to determine its position measured with another system relative to another frame, the positions of the points constituting one frame relative to those constituting another being known. Of

course, it is unnecessary here to state these relations, but attention should be drawn to the law that there are such general relations, and that the position of a point can be determined relative to *any* frame of reference by means of the coordinates appropriate to the form of that frame.

4. It must now be asked whether these laws, which make possible the measurement of position as a derived magnitude, are geometric laws, belonging to the study of rigid bodies and deducible from the fact that there are measurable geometric magnitudes, or whether they are new laws independent of that study. The second law, namely, that on which is based—in some manner that we have yet to discuss—the statement that space is three-dimensional, is clearly a new law; there is nothing whatever in the laws which determine the measurement of lengths and angles to tell us how many lengths and angles, based on any frame of reference, are necessary to fix a point. The first law, on the other hand, may seem at first sight to be nothing but a special case of the law of equality for lengths and angles—namely, that the relation of equality is transitive and symmetrical. But a little inquiry will show that something more is involved; it is the proposition that we might express now by saying that the distance between two points is not altered by the mere intervention of a solid obstacle. For, with our present conceptions, it is conceivable that all calipers might be changed in the same way by the insertion of various bodies between their tips, the change depending on the body inserted. The manner in which we have defined distance, involving the use of calipers, makes that expression and suggestion meaningless: the only way in which we can state the law is by the assertion that all propositions which are true of distances that can be measured directly by the introduction of a straight line are true also of distances that have to be measured indirectly by means of calipers—together with a similar assertion for angles. That is an extremely important proposition, which is not a mere consequence of the law of equality.

Similarly with the laws asserting equivalence of different systems of measurement. It is true that the relation between the Cartesian coordinates of a point on a cube, referred to the faces of a cube meeting at a corner, and the tetrahedral coordinates, referred to the four corners in which those faces meet, must follow from the geometry of the cube, this geometry being a consequence of the laws of measurement of the magnitudes and of the existence of cubes. But the fact that we can cut away most of the cube in any manner,

leaving enough to support the point and frame of reference, and still find the same relation to hold—that fact is new and not implied in solid geometry as we interpret it. If it is true, as we might say now, that “space is not distorted by the presence of matter in it,” that is a law which can only be established by experiment; it might be untrue and yet, so far as we can see, the laws of geometry, asserting the properties of rigid bodies, might yet remain unaltered.

5. Position then is a magnitude derived, like other derived magnitudes, from laws, some of which are numerical, some not. These laws include the geometric laws, but include also others which are distinctive laws of position. Position differs from all other derived magnitudes (I believe) because it is not a constant in the numerical laws on which it is based; it differs from most, if not all, others, because positions cannot be arranged in a one-dimensional series; otherwise it resembles them.

Now let us turn to space. If the æther is the subject of the verb to undulate, then space is the object of the verb to occupy. In experimental science space is that which is occupied by matter. The conception arises from a contemplation of the positions which actually occur. Let us examine any collection of rigid bodies, including the frame of reference, surrounded by air. If all these bodies are at relative rest (that is to say, the distance between every pair of points remains unaltered during the examination); and if we measure the positions of all the points we can define in such a system; then we shall find that only a very small proportion of the positions possible according to our system of measurement actually occur; we do not even find all values within a given range in all possible combinations. (It must be remembered that, in virtue of the step in fundamental measurement, the number of values is finite.) If we permit ourselves to introduce new rigid bodies, still leaving the old ones fixed, we can add very considerably to the number of positions that we can measure; but however many we introduce there will be some that cannot be measured. These missing positions may appear, however, if we change the relative positions of the original bodies. With any set of bodies we can discover rules, very complicated it may be, relating the positions that do occur (Class A) to those which can be made to occur (Class B) and those that cannot be made to occur (Class C). There is a certain complicated sense in which members of Class B and of Class C lie numerically between pairs of members of Class A, and this sense is rather different for Classes B and C. But

it is unnecessary to elaborate. Such facts as these, universally known, but immensely tedious to state formally, lead us to the idea that there are potential positions corresponding to all possible values of the coordinates, but that those of Class C are occupied by matter, those of Class B are not occupied at all, while Class A are those which lie on the boundary between occupied and unoccupied regions.

But what can be meant by a potential position which is not an actual position? If position is a measurable magnitude, anything that is not measurable is not a position. For it is no mere accidental limitation which prevents us from measuring positions occupied by a solid body; if there were no solid bodies which prevented us from measuring certain positions there would be no fundamental magnitudes by means of which we could measure them. The facts which distinguish potential and actual positions are facts inextricably involved in the concept position. Potential position is not therefore a concept; if it has any meaning for experimental science, it must be a hypothetical idea and any proposition in which it is involved must be a theory\*.

6. Let us then attempt to state in outline a theory by means of an "hypothesis" and "dictionary," the two parts of which, as I have concluded in a full discussion of the matter, every theory must consist. The hypothesis must state the properties of space. It consists of two parts. The first, concerned with the properties of pure space, is the set of propositions elaborated in any treatise on analytical metrical geometry. For the time being, we will suppose that the hypothetical space is three-dimensional and Euclidean. The conception of an infinite three-dimensional continuum of points is introduced, each point being a set of values of each of the three coordinates. Lines, surfaces, and spaces or regions are defined as collections of points between the coordinates of which certain analytical relations exist: distances between points, lengths of lines, areas of surfaces, and volumes of regions are defined as certain functions of these related coordinates. These and other similar definitions are shown to be mutually consistent, and from them are deduced by mathematical reasoning the whole series of propositions. The second part states the relation between space and matter; the most fundamental proposition, and the

\* Perhaps it will be well to explain once more that by "hypothetical" and "theory" I do not attach the slightest connotation of doubt. Some hypothetical ideas seem to me more obviously valid and some theories more obviously true than any concepts or laws.

only one involved in the simplest theory of space, is that space can be occupied by matter.

The dictionary connects these hypothetical ideas (points, related sets of points, and occupation by matter) with experimental concepts. It states that the proposition that space is occupied by matter means that there are positions of Class A, measurable and distinguishable from those of Classes B and C which are not measurable. In order to translate propositions asserting that certain specified points (and not merely some points) are occupied, it is necessary to introduce the frame of reference, and consequently the full entry in the dictionary becomes very elaborate. But, roughly, it states that, when it is said that certain points P are occupied and others Q are not, it is meant that a frame of reference and measurable coordinates can be so chosen that the values of the positions in Classes C and B are equal to the hypothetical coordinates of the points P and Q respectively, while those of Class A are equal to the coordinates of the hypothetical surface or surfaces separating P from Q.

The important proposition is here involved that all positions lie on hypothetical surfaces, while no occupied point corresponds to a position; positions do not form a continuum and are certainly not three-dimensional. It is therefore a matter of some difficulty to describe concisely the correlation between the physical point of which the position is measured and the hypothetical point which it is sometimes said to occupy, and to state accurately in terms of hypothetical points the important relation between contiguous physical points. It is important to realize that there is a difficulty and that the matter is not quite so simple as it appears at first sight; but it can be overcome. And when it is overcome, we can proceed to inquire whether the theory is true and predicts and explains true laws. The answer is (or was) that it is true, and that it predicts the laws of experimental geometry; further, it explains them in so far as the conception of a rigid body, always occupying mathematically similar regions, is acceptable and inherent in the fundamental ideas of the theory.

Further, as with all valuable theories, slight additions to the hypothesis and dictionary enable the theory to explain laws other than those on which (as we are supposing) it was originally based. By modifying slightly the idea of occupation, as defined by the dictionary, so as to permit occupation by incompressible fluids as well as by rigid bodies, we can explain the very important law relating the volume of a rigid

*Phil. Mag.* S. 6. Vol. 46. No. 275. Nov. 1923. 3 T



body, measured as a fundamental magnitude by means of Archimedes' laws, to the form of its surface. Again, by associating constants with the hypothetical points occupied by a body, these constants being properties of that body, we can explain the laws which involve (in our usual language) the interior of a body ; the law of density, for example, or the laws of thermal or electrical conduction. It should be noticed that the proposition that these hypothetical constants are properties of the occupying bodies and not of the region which they occupy is equivalent to the assertion of the homogeneity of space.

And one more step is taken when there are introduced hypothetical magnitudes, similar to these constants, associated with points that are not occupied by matter. Thereby we pass from action at a distance to action through a medium, and reach the characteristic theories of 19th century physics. Of all these theories, the theory of space is an essential part ; indeed, they may be regarded as successive extensions of the theory of space.

7. My object in presenting these considerations is to draw attention to the relation of the hypothetical idea of space to the experimental facts on which it is founded, and in particular to the experimental facts of geometry. But of recent years, as we all know, the theory of space is supposed to have undergone considerable change in connexion with the principles of relativity. Although it is not immediately relevant to my main purpose, it may be well to consider briefly how some of the new doctrines are to be interpreted according to the view put forward.

The chief of these doctrines, for our purpose, are that space is not absolute, but relative, and that, in the neighbourhood of massive objects, it is not Euclidean. Whether these doctrines are necessary consequences of those parts of the theory of relativity which have received experimental confirmation is a matter beyond our present inquiry ; let us assume for the moment that they are. What precisely are the alterations that they involve in the older theory ?

That position is relative is not a matter of theory at all ; it is involved in the meaning of position. The measurement of position requires both the use of a frame of reference and the law that all frames are equivalent according to certain laws. Again, there is nothing new in the doctrine of the homogeneity of space, which makes it impossible experimentally to identify a point except by its relations to other points on the surface of occupied regions. On the other hand, the

older theory was absolute in the sense that it required the individuality of the hypothetical points; unless the conception is admitted that the points, though experimentally indistinguishable, were individual and ideally distinguishable, it is impossible, so far as I can see, to state the hypothesis and to frame the dictionary in any intelligible manner. Many, perhaps most, theories contain some hypothetical ideas not determinable experimentally; to deny validity to such ideas is to reject all theoretical physics. The absoluteness of space, in this sense, is an essential part of the theory of space; a purely relative space, in which points have no identity, is simply not space at all—unless the practice is admitted of transferring names to new concepts which have nothing in common with those to which they were formerly attached.

It is agreed universally to-day that a hypothetical non-Euclidean space is possible. Certain definitions of Euclidean space can be changed—in particular, that defining the distance of two points in terms of their coordinates,—the others remaining unaltered; and a new scheme of definitions can be set up, self-consistent and leading to a new series of propositions differing from the old, but closely analogous to them. If we leave the dictionary unaltered, the new theory will, of course, predict correspondingly different laws; the two theories may be compared and tested by experiment. In particular, if the portion of the dictionary dealing with the occupation of space by matter is left unaltered, the theory will predict laws of experimental geometry other than the Euclidean.

But it must be remembered that, if this part of the dictionary is left unaltered, other parts must be altered. Any parts referring to rigid bodies, or to either of the three fundamental geometrical magnitudes, must be altered, because these concepts derive their validity from the Euclidean laws. If those laws are not true, there are no rigid bodies, no lengths, no angles, no areas, in the sense in which those terms are used at present in experimental science. It might be possible, by a consideration of the laws, deduced from the new theory, which would take their place, to establish new concepts corresponding to those which would have to be abandoned, and to make new entries in the dictionary involving these new concepts in place of the old. But until the experiments can actually be tried, any such proceeding would be exceedingly dangerous. Imaginary experiments are a terrible pitfall. Until they can be tried,

all guesses at the relations between "lengths" of "rigid" bodies occupying a non-Euclidean space should be regarded with the utmost suspicion.

When they are made as a result of the theory of relativity, such guesses are even more precarious ; for here there seems no reason to believe that the substitution of a non-Euclidean for an Euclidean space in the hypothesis would leave any part of the dictionary unaltered. For the theory of relativity demands alterations in the dictionary ; it demands not mere additions, as most previous theories have done, but the actual rejection of some entries previously accepted. But if one part of the dictionary is to be altered, what evidence is there that the remainder is to be left unchanged ? The denial that the length of a straight line is the distance between the extreme hypothetical points that it occupies is no more startling than many others that we now accept. But, further, the prediction from the theory of relativity of any laws of experimental geometry can be supported only if most of the dictionary is to be left in its accustomed form. Any changes in those laws predicted by the theory are far too small to be detected by actual measurements of the fundamental magnitudes by the methods on which their definition depends ; they can be predicted only on the assumption that there are other methods of measuring these magnitudes, which are equivalent to the fundamental method. But this equivalence depends on various laws deducible from the older theory of space, with the older hypothesis and the older dictionary. They will not be equivalent if other laws are substituted, deducible from a new theory with a new hypothesis but the old dictionary ; if they are to remain equivalent every entry in the dictionary must be appropriately revised. But if all others are to be revised, why should that relating to the occupation of space remain totally unaltered ? I conclude that, even if the theory of relativity demands a hypothetical non-Euclidean space, there is no reason to suppose that, even if experiments of infinite accuracy could be made, the laws of experimental geometry would take the corresponding non-Euclidean form or that they would not remain truly Euclidean.

CVII. *The Electronic Theory of Valency.*—Part III. *The Transmission of Chemical Affinity by Single Bonds.* By Professor T. MARTIN LOWRY, C.B.E., M.A., D.Sc., F.R.S.\*

1. *Transmission of Chemical Affinity by Single Bonds and by Conjugated Systems.*

IT is now generally recognized that chemical affinity can be transmitted through chains of atoms in two different ways. In the first case, one atom exerts on another an effect which is always of the same kind, although it may diminish rapidly as the distance between the atoms increases. In the second case, alternate atoms are affected in opposite ways, in accordance with Lapworth's "Principle of Alternate Induced Polarities" †. The electronic mechanism underlying this alternation of polarities has been discussed in Part II. of this series of papers ‡. The mechanism of transmission of affinity through single bonds (Lapworth's "General Effect") has been discussed briefly in Part I., as depending on a possible displacement of the nuclei relatively to the enveloping shells of electrons. The object of the present communication is to inquire whether these two mechanisms are sufficient to explain all the facts in reference to the transmission of chemical affinity through chains of atoms, or whether there is a residue of unexplained observations which demand yet another mechanism to account for them. The invention of a third mechanism would probably not present any great difficulty; but very clear proof of the real existence of an "unexplained residue" of facts must be forthcoming before the necessity of such an invention can be admitted. In the opinion of the writer the existence of this residue is still unproved.

2. *Are Alternate Polarities possible in Saturated Systems.*

In general, the theory of polar double-bonds does not allow of any extension of alternate polarities beyond the last double bond of a conjugated system, since "on every occasion where the sign + — is written a bond must be deleted in the conventional formulæ" (Trans. Chem. Soc. cxxiii. p. 824 (1923)). Lapworth § has, however, called

\* Communicated by the Faraday Society.

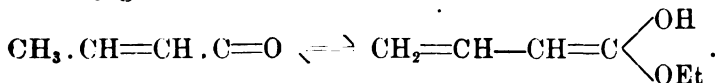
† Manchester Memoirs, lxiv. No. 3 (1920).

‡ Compare Trans. Chem. Soc. cxxiii. p. 822 (1923).

§ *Ibid.* p. 4.



crotonate may depend on an enolization which, according to the principles of Thiele, should affect the terminal groups of the conjugated chain thus :



A real test of the extension of alternate polarities to single bonds must obviously be made on atoms at such a distance from the conjugated chain (*e.g.* in a  $\delta$ -position) as to be exempt from the possibility of changes such as the one set out in the preceding equation ; no such test appears to have been described hitherto.

### 3. Strong and Weak Bonds in Saturated Compounds.

Somewhat similar conclusions as to alternation in chains of single bonds have been reached from another point of view by Flürscheim \*, who adopts the view of Claus † that "the force with which two atoms are linked is not a constant, but that, depending on the nature of the other atoms in the molecule, it must be assumed to vary from compound to compound." The strengthening of one bond is supposed to weaken the next, and conversely ; a single unsaturated atom is therefore able to develop alternate strong and weak bonds throughout a chain of atoms, and this effect is not limited to conjugated chains, but may also occur in chains that are otherwise completely saturated. There would be no difficulty in expressing this view in terms of the electronic theory ‡ ; but a critical review of the experimental facts is needed before the necessity for the introduction of an additional mechanism can be accepted.

### 4. Dissociation-Constants of Halogenated Fatty Acids.

Table I. shows the dissociation-constants of a series of halogenated acids at 25°. It will be seen that the influence of the halogen falls off rapidly as it is moved from an  $\alpha$ - to a  $\delta$ -position, where its effect practically disappears. In this case at least there is no slightest sign of alternation. This would, I think, be explained by Flürscheim on the ground that the halogens are strongly polar but not strongly unsaturated.

\* Trans. Chem. Soc. xcv. p. 718 (1919).

† Ber. xiv. p. 432 (1881).

‡ Compare Kermack and Robinson, Trans. Chem. Soc. cxxi. p. 431 (1922).

TABLE I.

Dissociation-Constants ( $\times 10^5$ ) of Halogenated Acids at 25°.

	$\alpha$ .			$\beta$ .			$\gamma$ .			$\delta$ .			No Halogen.
	Cl	Br	I	Cl	Br	I	Cl	Br	I	Cl	Br	I	
Acetic .....	155	156	75	...	...	...	...	...	...	...	...	...	1.8
Propionic.....	147	108	...	8.6	9.8	9.0	...	...	...	...	...	...	1.4
Butyric .....	139	106	...	8.9	...	...	3.0	2.6	2.3	...	...	...	1.5
Valeric.....	...	...	...	...	...	...	...	...	...	1.9	1.7	...	1.6

CH<sub>3</sub>.CO<sub>2</sub>H 1.8 ; CH<sub>2</sub>Cl.CO<sub>2</sub>H 155; CHCl<sub>2</sub>.CO<sub>2</sub>H 5000  
 CCl<sub>3</sub>.CO<sub>2</sub>H 30,000; CH<sub>2</sub>Br.CHBr.CO<sub>2</sub>H 670; CH<sub>3</sub>.CBr<sub>2</sub>.CO<sub>2</sub>H 3300.

5. *Dissociation-Constants of Unsaturated Acids.*

Flürscheim relies for part of his evidence on the unsaturated acids. The data for these are set out in Table II. (a), where the dissociation-constants of the  $\beta\gamma$  unsaturated acids are seen to be higher than those of the  $\alpha\beta$  or  $\gamma\delta$  acids.

TABLE II.

(a) <i>Unsaturated Acids.</i>					<i>Saturated Acids.</i>		
	$\alpha\beta$ .	$\beta\gamma$ .	$\gamma\delta$ .	$\delta\epsilon$ .			
C <sub>2</sub> H <sub>4</sub> .COOH	5.60	...	...	...	H.CO <sub>2</sub> H	21.4	C <sub>2</sub> H <sub>5</sub> .COOH 1.43
C <sub>3</sub> H <sub>5</sub> .COOH	2.0	...	...	...	CH <sub>3</sub> .COOH	1.8	C <sub>3</sub> H <sub>7</sub> .COOH 1.5
	3.6	3.8	...	...			
	(iso.)						
C <sub>4</sub> H <sub>7</sub> .COOH	1.48	3.35	2.09	...	C <sub>2</sub> H <sub>5</sub> .COOH	1.4	C <sub>4</sub> H <sub>9</sub> .COOH 1.6
$\alpha$ Me	1.1	3.0	2.16	...			
$\beta$ Me	0.73	2.88	...	...			
$\alpha$ Et	2.05	3.39	...	...			
C <sub>5</sub> H <sub>9</sub> .COOH	1.89	2.64	1.74	1.91	C <sub>3</sub> H <sub>7</sub> .COOH	1.5	C <sub>5</sub> H <sub>11</sub> .COOH 1.45
(b) <i>Saturated Acid, Vinyl-derivative, Chloro-derivative.</i>							
Formic acid .....	21.4	5.60	Not known.				
Acetic acid .....	1.8	3.8	155				
Propionic acid .....	1.4	2.09	88.6				
Butyric acid .....	1.5	1.91	3.0				
Valeric acid .....	1.6	...	1.9 (Br)				
(c) <i>Formic Acid, Acrylic Acid.</i>							
H.CO <sub>2</sub> H	21.4	H.C <sub>2</sub> H <sub>2</sub> .COOH	5.6				
CH <sub>3</sub> .COOH	1.8	CH <sub>3</sub> .C <sub>2</sub> H <sub>2</sub> .COOH	2.0 or 3.6				
			cis? trans?				
C <sub>2</sub> H <sub>5</sub> .COOH	1.4	C <sub>2</sub> H <sub>5</sub> .C <sub>2</sub> H <sub>2</sub> .COOH	1.48				
C <sub>3</sub> H <sub>7</sub> .COOH	1.5	C <sub>3</sub> H <sub>7</sub> .C <sub>2</sub> H <sub>2</sub> .COOH	1.89				
C <sub>4</sub> H <sub>9</sub> .COOH	1.6						

Two alternative ways of regarding these acids may, however, be submitted. Thus in Table II. (b) the saturated

acids of the series  $H \cdot C_nH_{2n} \cdot CO_2H$  are compared with their vinyl derivatives,  $CH_2 : CH \cdot C_nH_{2n} \cdot CO_2H$ , in order to bring out the effect of the unsaturated vinyl group as a substituent. This table shows that, except in the case of formic acid, the vinyl group increases the acidity of the compound, although less strongly than a halogen, but without showing any signs whatever of alternation. In Table II. (c) the corresponding derivatives of formic acid,  $R \cdot COOH$ , and of acrylic acid,  $R \cdot CH : CH \cdot CO \cdot OH$ , are compared. This table shows in a remarkable way that, in both series of compounds, the diminution of acidity by the chain of carbon atoms is most marked at the ethyl-derivative, where the dissociation-constant passes through a minimum in each case. The table therefore suggests that the effect of the growing chain is handed on through the  $-CH=CH-$  group to the carboxyl-group, but by a mechanism in which the two unsaturated carbon atoms act as excellent transmitters, but do not themselves count as a part of the chain\*. The only way in which any alternation of properties can be detected in this series of acids is by tracing out the effect of moving the double bond along the chain. Even then the alternations are only of the same order of magnitude as those produced by *cis-trans* isomerism, *e. g.* in crotonic acid. It is therefore quite possible that these small fluctuations are steric in origin, depending on some question of the configuration of the chain, rather than on a reversal of polarity in alternate atoms.

#### 6. Acylous and Basyulous Groups.

It is usual to describe radicles which increase the strength of an acid as negative, whilst those which decrease acidity are called positive. Lapworth † regards these as misnomers, since when acetamide is hydrolysed the "positive"  $-NH_2$  attracts the positive hydrogen ion, whilst the "negative"  $-CO \cdot CH_3$  attracts the negative hydroxyl. A similar contradiction in terms is implied in describing chlorine as a "negative" radicle because it repels a positive hydrogen ion in hydrogen chloride. Lapworth therefore proposes to use the terms "acylous" and "basyulous" instead of "negative" and "positive." These terms are, however, merely relative, since they describe the change produced on introducing one radicle in the place of another. The displaced radicle

\* This is also in harmony with Lapworth's observation on ethyl crotonate.

† Manchester Memoirs, lxiv. No. 3, p. 2 (1920).



is usually hydrogen, and according to the common view  $-\text{CH}_3$  and  $-\text{NH}_2$  are positive or basylous, whilst  $-\text{OH}$  and  $-\text{Cl}$  are negative or acylous. This view is also open to criticism on grounds set out below.

7. *Directly-attached Hydrogen as an Acylous Group.*

The dissociation-constants of a series of saturated fatty acids are set out in Table III.

TABLE III.

Dissociation-Constants ( $\times 10^5$ ) of Fatty Acids.

$\beta$ .	$\alpha$ .		$\gamma$ .	$\beta$ .	$\alpha$ .		
	H . CO . OH	21.4		CH <sub>3</sub> . CH <sub>2</sub> . CH <sub>2</sub> . CO . OH		1.5	
	CH <sub>3</sub> . CO . OH	1.8		CH <sub>3</sub> > CH . CH <sub>2</sub> . CO . OH		1.7	
CH <sub>3</sub> . CH <sub>2</sub> . CO . OH		1.4		CH <sub>3</sub> > CH . CH <sub>2</sub> . CO . OH		1.7	
CH <sub>3</sub> > CH . CO . OH		1.4		CH <sub>3</sub> . CH <sub>2</sub> > CH . CO . OH		1.7	
CH <sub>3</sub> > CH . CO . OH		1.4		CH <sub>3</sub> . CH <sub>2</sub> > CH . CO . OH		1.9	
CH <sub>3</sub> > C . CO . OH		1.0					
			$\epsilon$ .	$\delta$ .	$\gamma$ .	$\beta$ .	$\alpha$ .
					CH <sub>3</sub> . CH <sub>2</sub> . CH <sub>2</sub> . CH <sub>2</sub> . CO . OH		1.6
					CH <sub>3</sub> . CH <sub>2</sub> . CH <sub>2</sub> . CH <sub>2</sub> . CH <sub>2</sub> . CO . OH		1.46

There is a very big drop in acidity on passing from formic to acetic acid; but if  $-\text{CH}_3$  were really a basylous group, there should be a cumulative decrease of acidity in mono-, di-, and tri-methylacetic acids, analogous to that recorded in the case of the chloroacetic acids. Actually, the replacement of  $-\text{H}$  by  $-\text{CH}_3$  has very little effect on the strength of acetic acid; and when the replacement takes place at a still greater distance from the carboxyl, the sign of the effect is reversed, since the dissociation-constants of the normal fatty acids pass through a minimum at propionic acid followed perhaps by a shallow maximum at *n*-valeric acid. Under these conditions it is much more reasonable to think of  $-\text{CH}_3$  as a neutral radicle, at least when studying the series of fatty acids, and to regard the directly attached hydrogen atom of formic acid as definitely acylous.

8. *Acylous Character of the Amino-Group.*

Much confusion has arisen from the idea, which is held almost universally, that the amino-group is strongly basylous. This is incorrect, and evidence is set out below to show that, when its direct neutralizing action is eliminated, it possesses well-defined acylous properties. This view was suggested by Vörlander in 1902\*, but has failed to secure the general acceptance which it deserves. Thus Flürscheim's paper was written mainly in order to account for the "anomaly" that amino-acids are sometimes stronger than the fatty acids from which they are derived. If, however, the amino-group is really acylous, this must be a perfectly normal effect, although it is commonly masked by the formation of internal salts.

TABLE IV.

Dissociation-Constants ( $\times 10^5$ ) of Anilino-acetic Acid, etc.

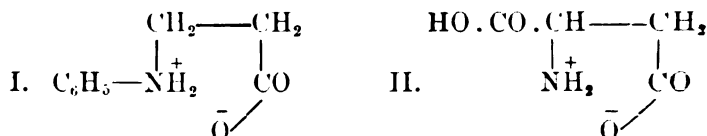
$\text{C}_6\text{H}_5 \cdot \text{O} \cdot \text{CH}_2 \cdot \text{COOH}$	76	$\text{C}_6\text{H}_5\text{N} \begin{cases} \text{CH}_2 \cdot \text{COOH} \\ \text{CH}_2 \cdot \text{COOH} \end{cases}$	270
$\text{C}_6\text{H}_5 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{COOH}$	3.9		
$\text{C}_6\text{H}_5 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$	2.3	$\text{C}_6\text{H}_5 \cdot \text{CH} \begin{cases} \text{CH}_2 \cdot \text{COOH} \\ \text{CH}_2 \cdot \text{COOH} \end{cases}$	7.7
$\text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$	1.4		
$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{COOH}$	1.4	$\text{CH}_2 \begin{cases} \text{CH}_2 \cdot \text{COOH} \\ \text{CH}_2 \cdot \text{COOH} \end{cases}$	4.7

Table IV., most of which is quoted from Vörlander, shows that the  $-\text{NH}-$  group occupies, as might be expected, an intermediate position between  $-\text{CH}_2-$ , which is practically neutral, and  $-\text{O}-$ , which is strongly acylous. In this series of acids, the tendency of the basic amino-group to absorb the hydrogen-ions as fast as they are set free by the carboxyl, is reduced to a minimum by the influence of acylous substituents on the nitrogen. Evidence of a similar character is provided by studying the influence of the amino-group on a base where no question of neutralization can arise; the acylous character of the group is then shown by the fact that hydrazine is a weaker base than ammonia.

Exceptional behaviour may be expected when the formation of an internal salt involves the formation of a 5-atom

\* *Ann.* 520. p. 99 (1902).

ring as in  $\beta$ -anilino-propionic acid I. or in amino-succinic acid II.



In the former case very complete neutralization occurs, and  $\beta$ -anilino-propionic acid ( $0.4 \times 10^{-5}$ ) is weaker than propionic acid ( $1.4 \times 10^{-5}$ ), whereas  $\alpha$ -anilino-propionic acid ( $3.8 \times 10^{-5}$ ) is stronger; but it is the weak and not the strong acid that is the anomaly. In the latter case, amino-succinic acid is stronger than succinic acid, although  $\alpha$ -amino-acetic acid is weaker than acetic acid. The strength of amino-succinic acid arises from the fact that the direct neutralizing action of the amino-group is fully used up by the carboxyl-group with which it forms a five-atom ring; the other carboxyl-group therefore shows the normal increase of acidity produced by an acylous substituent, undisguised by any neutralizing action.

If this view of the acylous character of the amino-group be adopted, the anomalous behaviour of the amino-acids appears to be perfectly normal and the special mechanism devised by Flürscheim to account for it is no longer needed.

### 10. Summary.

(a) The reactivity of the methyl-group in ethyl crotonate is in harmony with the theory of polar double bonds. It cannot be used as a proof of the existence of polarized single bonds (polar covalencies), since it receives a simple interpretation in terms of Thiele's theory of conjugation.

(b) The small fluctuations which are observed in the strength of unsaturated acids as the double bond is moved along the chain may be attributed to steric influences such as those which Pickard has discovered in optically active compounds.

(c) The fact that amino-acids are sometimes stronger than the acids from which they are derived is attributed to the acylous character of the amino-group; this is usually masked by the direct neutralizing action of the basic group.

(d) The conclusion is drawn that alternate polarities are characteristic of conjugated systems, and that it is not yet proved that they can be developed in chains of single bonds, where both acylous and basylous groups produce effects of constant sign.

University Chemical Laboratory,  
Cambridge.

CVIII. *Notices respecting New Books.*

- (1) *Physics, the Elements.* By N. R. CAMPBELL. Pp. vii+565. Cambridge University Press. 40s. net.
- (2) *Modern Electrical Theory*, Chapter xvi., Relativity. By N. R. CAMPBELL. Pp. vi+116. Cambridge University Press. 7s. 6d. net.

(1) **A**T the beginning of the first of these books it is stated that the main object is to be analysis of physics, especially with a view to ascertaining the nature of the available evidence and the meaning and reliability of the results based upon it. The need for such analysis is plain. The discussions of Mach and Pearson are good so far as they go, but they are only a beginning. A book with this object, consisting of over 500 large pages, and written by an experimental physicist with a wide knowledge of modern physical developments, might have been expected to make advances of the greatest importance in the understanding of scientific processes. There are notable contributions to the descriptions of some of these processes, but none to the understanding of scientific inference and the reasons why some judgments are considered more reliable than others.

The reason for the failure is foreshadowed on p. 3. "These inquiries will be clearly the more interesting the more fundamental are the propositions and the ideas concerning which they are made . . . it will not be our object to raise doubts concerning them; it will be rather to examine why no doubts are possible . . . . Least attention of all will be required for these branches of our knowledge where opinion is still not wholly agreed; to examine in detail propositions which may yet be rejected would be waste of time." It is, however, just precisely the propositions that are in doubt that constitute the most interesting part of science; every scientific advance involves a transition from complete ignorance, through a stage of partial knowledge based on evidence becoming gradually more conclusive, to the stage of practical certainty. By limiting his discussion to the last stage, when he thinks "no doubts are possible," Dr. Campbell has excluded from consideration everything that most interests the ordinary physicist.

It is, of course, a logical commonplace that however many instances of a general proposition may have been verified, it is impossible to infer anything whatever, either with certainty or with probability, about the result of the next attempted verification, unless we have some other general proposition to guide us.

This general proposition must evidently be accepted *a priori*. Many writers have avoided the difficulty by attempting to deduce the properties of the world from general propositions alone, which they think they know *a priori*, regarding experiments as an adventitious luxury. Dr. Campbell, on the other hand, wishes to reduce everything to experiment, excluding all *a priori* postulates, and yet to be able to make inferences. This being inconsistent with logic, he is led to deny the logical proposition altogether denying that any general proposition is used in scientific method. Thus we have on p. 112, "There is no method, and it is because there is no method which can be expounded to all the world that science is a delight to those who possess the instincts which make methods unnecessary," and on p. 354, "Such laws . . . . cannot be discovered by any formal process; they can only be suggested by some considerations for which no formal rule can be laid down and then shown to be in accordance with experiment. There is no such thing as formal induction."

This obscurantist position naturally leads the author into an attack on logic and mathematics, which he wishes to make irrelevant to science. In particular, he attempts to distinguish between the number (small *n*) of a class, and the mathematical Number (capital *N*) defined as a class of classes. This arises from a misunderstanding, not a surprising one in view of Mr. Bertrand Russell's semipopular expositions. Whitehead and Russell take as fundamental the notion of the comparison of two classes, members being selected in pairs, one from each class, a class being greater than the other if it has any members left unpaired when the other is exhausted. This is precisely Dr. Campbell's definition. The notion of a class of classes is not defined by Whitehead and Russell; they give instead an interpretation of every proposition involving it, these interpretations being such that the class of classes will have the same fundamental properties as are believed to be possessed by the number of a class, and such that formal logical development from them is possible. Consequently every proposition true of number is also true of Number, and *vice versa*. In the only sense that conveys any meaning they are therefore the same thing.

Again, Dr. Campbell suggests that the mathematical notion of function does not occur in physics, since all functions can be represented by graphs or calculated by machines, both processes being purely physical. But the use of analogy with a graph or a machine is itself a logical process, so that these devices do not avoid logic; they merely lower its quality. Further, the 0.3 per cent. accuracy possible in a graph is ridiculously inadequate for the representation of the accuracy of many known physical laws; and the process of grinding out the value of  $\cos x$ , term by term, on a machine can hardly be considered analogous to the way a

particle moves under a force to the origin proportional to the distance.

An analytic function is defined on p. 355 as "one which has a differential coefficient at each point of the range, except possibly a finite number of separate points." The possession of a differential coefficient at points of an *area* is one of the criteria for an analytic function of a *complex* variable, but differentiability for real values does not afford any criterion; and an analytic function may have an infinite number of singularities in a finite region. This definition appears as a footnote to a paragraph the last sentence of which is equally reliable.

A scientific law could reach a stage when "no doubts are possible" only if the *a priori* general propositions dealt with certainty and not with probability. I do not believe that they deal with certainty, for if they did there should be a stage in one's knowledge about a law when it passes suddenly from complete ignorance to complete certainty, which does not appear to be the case; and on the basis of probability inference it seems possible to establish laws with probabilities as great as are required for any ordinary scientific purpose. Dr. Campbell is, however, dissatisfied with probability inference, and wishes to attain certainty. Thus he is led into further difficulties.

He realizes the fallibility of the individual judgment, and his scheme therefore requires the substitution of something more reliable. He therefore introduces the concept of "universal agreement." Thus on p. 10 we read (A) "In science, but not in metaphysics, it is possible to obtain universal agreement for conclusions"; on p. 21 (B) "The subject matter of science may be defined as those immediate judgements concerning which universal agreement may be obtained"; on p. 216 (C) "There is a certain class of judgements concerning which universal agreement can be obtained as it can be obtained about no other class. These judgements are those about the association of sensations; not about the occurrence of sensations, . . . . but about their uniform association which determines action. These judgements if they were expressible explicitly at all would be expressed as laws, but since the ideas involved in them are more fundamental than any language they are not so expressible"; and on the same page (D) "we include only definite 'experiments' which can be repeated and can be shown to other observers." If statement C means anything it seems to contradict the use of the word 'conclusions' in A, and to imply that all persons react in just the same way to certain stimuli; and if these associations are the basis of physics these stimuli must include the spatial and temporal coincidences that physics deals with. The falseness of this statement is a commonplace of experimental psychology; the differences of the reactions of different persons to just these stimuli constitute the

subject matter of an elaborate science. Indeed they are unpleasantly familiar to all observational astronomers.

Even, however, if investigation had shown that judgments of some class were the objects of universal agreement, it would be impossible to utilize this knowledge with regard to a particular observation without the minor premiss that the particular proposition considered is an instance of the class which is a judgment possible only to the observer. The ultimate recourse to the fallible individual judgment is unavoidable.

Chapter VII. deals with probability, the Venn definition, concerning which enough has been said already, being adopted.

The establishment of any physical law is reduced to the pursuit of a further Snark. A law (p. 213) leaves the residuals in a random distribution. But they could not conceivably be distributed exactly at random unless they were infinite in number. Thus no law could ever be established at all, much less with the certainty Dr. Campbell demands. Incidentally the above test for a law makes errors methodologically prior to laws, and therefore they should have been discussed before them; actually they are considered three chapters later.

As a matter of fact the difficulty of reading the book is much increased by the author's habit of suddenly breaking off discussion of a point with a promise to return to it later, but with no indication of the place, if any, where he does return to it.

It must not be inferred from the above criticisms that the book is worthless. Chapters VIII. to XV. are for the most part very good, though they are often marred by errors arising out of those just pointed out. They deal with The Meaning of Science, Science and Philosophy, Fundamental Measurement, Physical Number, Fractional and Negative Magnitudes, Numerical Laws and Derived Magnitudes, Units and Dimensions, and the Uses of Dimensions. The notions of Fundamental and Derived Magnitudes probably constitute one of the chief advances in the subject yet made, and the discussion of dimensions is extremely illuminating. To attempt to discuss them here would, however, be useless. The book should be read.

Dr. Campbell's book must be regarded as pioneer work in an extremely difficult subject, and the best purpose such work can serve is to open up new fields for investigation. To stimulate thought is the first need; and it is impossible to read much of the book without receiving such stimulus. Most of the questions asked in this book are of the first importance; many of them are answered wrongly, but the great need of a new subject is to have the important questions asked; it is premature to hope for correct answers to all at the first attempt. When all the questions raised by Dr. Campbell have been answered, the theory of scientific method will be a well-developed science.

(2) Of the making of books on relativity there is no end. But the associated weariness of the flesh is less in this case than in most others. It is definitely addressed to those interested in relativity because it predicts something experimentally true; it is a book on physics and not on mathematics or philosophy. The author on the whole fulfils his object well. It is the most physical book on the subject yet published; completeness of argument has been sacrificed by the omission of many steps of algebra and calculus, but the reader can obtain these by referring to other works, Cunningham's 'Relativity and the Electron Theory' being the most likely to harmonize with Dr. Campbell's. Its chief purpose is to clear up the difficulties that physicists have experienced in dealing with the more mathematical expositions.

The special theory is derived from two principles, the first relating to the independence of laws of the motion of the observer, while the second is practically the usual  $ds=ds'$ . The Lorentz-Einstein transformation and the law of composition of velocities are derived from these. The Doppler effect, aberration, and the experiments of Fizeau and Michelson and Morley are then explained. The accounts of these physical experiments are the clearest I have seen (but on p. 27,  $2l/c$  has been written for  $2l/(c^2-v^2)^{\frac{1}{2}}$ , and on p. 30,  $q$  has several times been written for  $v$  without explanation).

At this stage the geometrical interpretation of Minkowski is introduced. The four-dimensional space-time, one coordinate being always imaginary, is regarded as a pure device for making the mathematics easier, which is, I think, the correct attitude. The general theory is then derived from this; though I think Dr. Campbell exaggerates the extent to which the general theory is hypothetical. In the summary he appears to be approaching tolerance of mathematics.

On p. 104, line 12, "less" should be "longer," and two lines below, "rod" should be "red." Misprints are very few in both books.

HAROLD JEFFREYS.

## CIX. *Proceedings of Learned Societies.*

### GEOLOGICAL SOCIETY.

[Continued from p. 719.]

May 2nd, 1923.—Prof. A. C. Seward, Sc.D., F.R.S., President, in the Chair.

Prof. JOHN JOLY, D.Sc., F.R.S., F.G.S., delivered a lecture on the Bearing of some Recent Advances in Physical Science on Geology.

After referring to the discovery by the present Lord Rayleigh of the general distribution of radioactive materials and to the *Phil. Mag.* 8. 6. Vol. 46. No. 275. Nov. 1923. 3 U



earlier but more recently developed discovery of isostasy, the Lecturer observed that, assuming that the dense layer upon which, according to the theory of isostasy, the continents float, is composed of basalt possessing the average radioactivity of basalts, it may be calculated that, if this substratum is now solid (as appears from both tidal and seismological evidence), it will have acquired sufficient radioactive heat to become fluid in about 30 million years.

The change of density then occurring will cause a downward motion of the continents relative to the ocean, and transgressional seas will result. After a long period, during which the liquid magma (under tidal forces) circulates from beneath the continents (which, owing to their own radioactivity, act as an adiatherminous covering) to suboceanic regions, the accumulated heat is given up to the ocean. Re-solidification of the magma ensues, and the restoration of the former higher density causes the continents to rise relatively to the oceans, and brings about the retreat of transgressional seas. In this manner, the complete cycle of a revolution finds explanation.

Mountain-building forces arising during the climax of revolution originate from two sources:—(a) the effects of the horizontal tide-generating force and of precessional force which, although probably considerable, have not yet been evaluated; (b) the effects of the changing area of the ocean-floor attending the expansion and contraction of the basaltic layer, whereby the oceanic area becomes alternately increased and diminished. Upon shrinkage the enlarged ocean-floor bears against the continents. Hence 'the highest mountains confront the widest oceans.'

Mountain-building is due much more to vertical than to horizontal forces. The mountains are not pushed up by lateral forces: these forces act upon the subsiding geosyncline to produce deformation of the semi-plastic materials. The mountains are elevated long after by the isostatic forces, the energy being traceable to the stored radioactive heat of prior ages.

Inter-revolutionary events consist of 'preparatory' disturbances, due to local increase of liquefaction of the magma: also of 'sequential' disturbances, due to relief of strain accumulated during revolution, and to the restoration of isostatic equilibrium.

The conditions now prevailing beneath the continents preclude the establishment of a steady state (that is, of thermal equilibrium), and in the past always must have done so.

The cyclical events outlined in the theory here adduced appear to be inevitable as a consequence of radioactivity and isostasy. Cyclical disturbances alone can explain the past history of the Earth's surface.

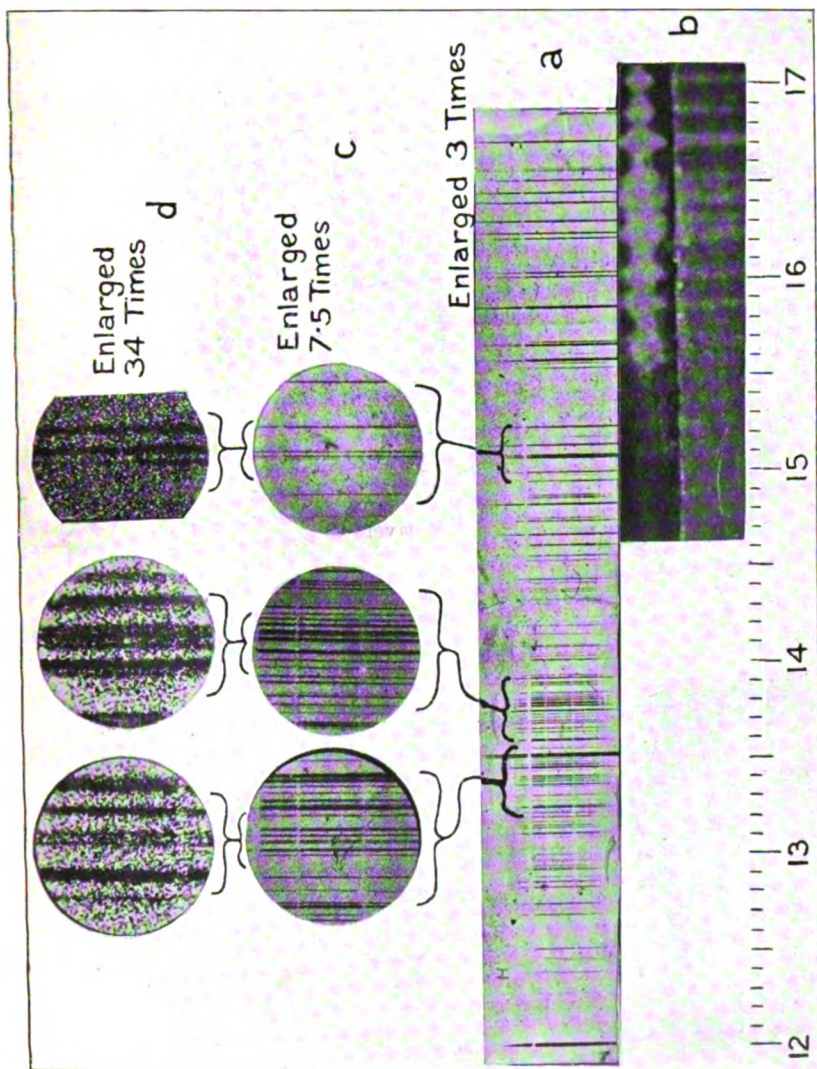




FIG. 8.

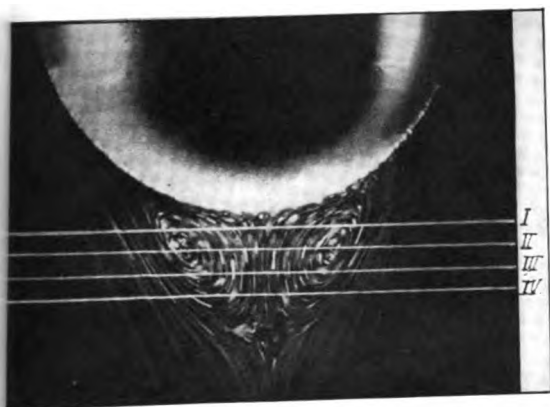


FIG. 11.



FIG. 14.

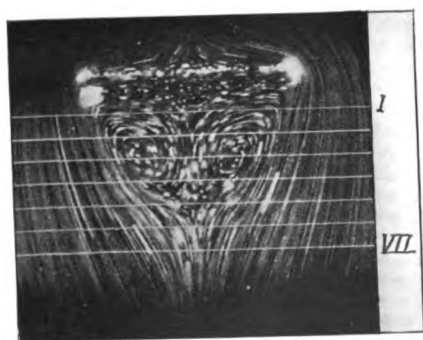
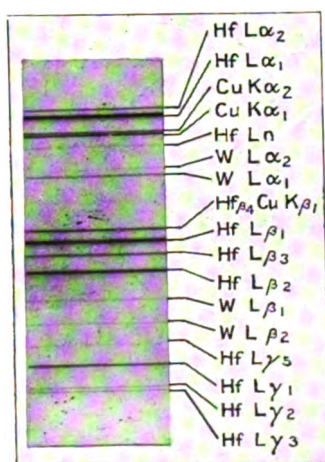


FIG. 15.







Hf L-SPECTRUM.



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[SIXTH SERIES.]

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DECEMBER 1923.

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(CX. *The Initial Motion of a Projectile.*

By E. T. HANSON, B.A.\*

[The Author is indebted to the Admiralty for permission to publish  
this paper.]

INTRODUCTION.

THE problem of a projectile's motion first attracted my attention some years ago in connexion with the theory of prediction in anti-aircraft gunnery. I did not, however, proceed at that time beyond obtaining the equations of motion under an arbitrary system of impressed forces.

Recently, upon reading a very interesting paper entitled "The Aerodynamics of a Spinning Shell," Phil. Trans. Series A, vol. cccxi., it occurred to me that the following application might be made of the force system, therein obtained by an ingenious combination of theory and experiment. The application referred to is based upon the remarkably simple forms which the most important forces acting upon a particular shell appear to take at high velocities. These forms are found to be applicable to the motion of the shell during the first seven or eight seconds of its time of flight, that is to say, during its "settling-down" period.

The shell mentioned is the 16 lb. 3-inch A.A. shell, but it may reasonably be assumed that shells of similar form will

\* Communicated by R. H. Fowler, M.A., of Trinity College, Cambridge.

be accompanied by corresponding simplicity in the forces which act upon them.

In Section 1, I have outlined the proof of the general equations of motion as I originally obtained them, and also the modified equations which are applicable to the problem under discussion. These equations are obtained by a different method in the paper referred to; hardly more is given, therefore, than is necessary to explain the notation used.

In Section 2, I have discussed shortly the initial portion of the plane trajectory, and the system of forces acting upon the shell over this portion.

In Section 3, I have considered the solution of the equations of motion during the period over which the force system is valid.

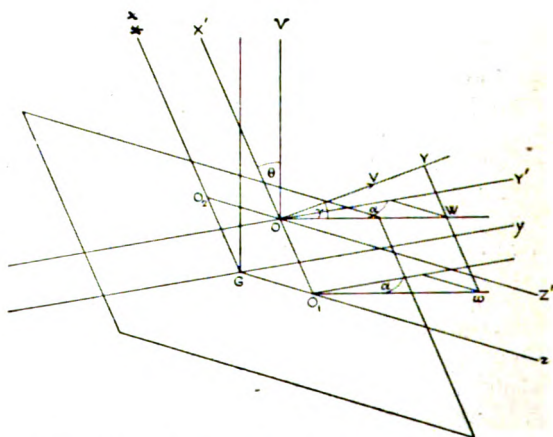
### Section 1.—THE GENERAL EQUATIONS OF MOTION.

#### *The Kinematics of the Motion.*

##### (a) *The motion of the centre of gravity.*

This motion is obtained relatively to a predetermined curve in space, which is known as the plane trajectory.

Fig. 1.



Let O (fig. 1) be the position of the centre of gravity of the projectile at any instant. Through O construct a plane perpendicular to the plane trajectory, and cutting the latter in G.

Let  $Gy$  be the tangent to the plane trajectory at G,  $Gx$  the normal, and  $Gz$  perpendicular to the plane of the plane trajectory. Through O draw axes parallel to  $Gx$ ,  $Gy$ ,  $Gz$ .

Let  $\theta$  be the angle between the vertical VO and Gx or OX'.

The motion of the centre of gravity O is referred to co-ordinate axes Gx and Gz in a moving plane which at every instant is perpendicular to the plane trajectory. This plane always contains O and must rotate about OZ' with angular velocity  $\dot{\theta}$ .

The coordinates  $x$  and  $z$  of O are convenient for determining the drift, but for the discussion of the actual motion of the centre of gravity other coordinates are more useful.

Let OY be the resultant direction of motion of the centre of gravity at the instant in question, and let the plane X'OY cut the plane Y'OZ' in OW.

$$\begin{aligned}\text{Let} \quad & \text{Y'OW} = \alpha \\ \text{and} \quad & \text{YOW} = \gamma.\end{aligned}$$

Let  $v$  be the resultant velocity of the centre of gravity along OY. The velocity of G along the tangent to the plane trajectory is

$$u = v \cos \alpha \cos \gamma - OO_1 \cdot \dot{\theta}. \quad . \quad . \quad . \quad (1)$$

Imagine a plane X'OO<sub>1</sub>cW to move with O in such a manner that O<sub>1</sub>c is at O<sub>1</sub> the tangent to a curve to be determined by the value of  $\dot{\alpha}$  and  $\frac{\partial}{\partial t}(v \cos \gamma)$ .

This curve would be plotted on a plane which can be considered to roll on the plane trajectory round the moving line Gz. In this way a cylindrical surface is constructed which always contains the centre of gravity.

In this cylindrical surface is plotted a curve to be determined by the values of  $v$  and  $\dot{\gamma}$ . The common origin of both these curves is coincident with that of the plane trajectory. The values found for  $v$ ,  $\dot{\alpha}$ , and  $\dot{\gamma}$  are sufficient to determine the whole motion of the centre of gravity.

(b) *The motion about the centre of gravity.*

In fig. 2 OXYZ is a system of rectangular axes drawn through the centre of gravity O of the projectile.

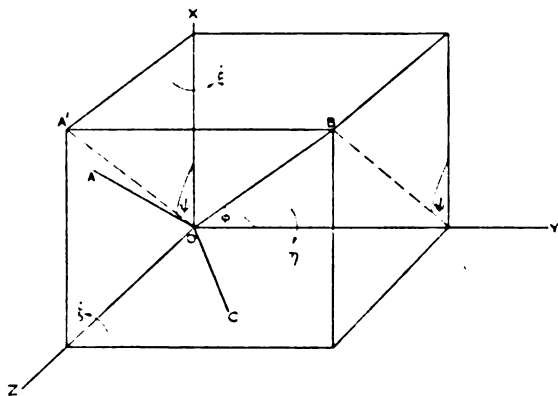
In the consideration of this part of the motion it is postulated:—

- (1) That at the instant under consideration the centre of gravity O is moving in the direction OY.
- (2) That the axes OX, OY, OZ are instantaneously turning about themselves with angular velocities  $\xi, \eta, \zeta$ , which are right-handed on looking along OX, OY, and OZ respectively from the origin.

Let  $OB$  be the axis of the projectile, making an angle  $\phi$  with  $OY$ .  $\phi$  is called the "yaw" of the shell and  $BOY$  is the plane of yaw, which makes an angle  $\psi$  with the plane  $XOY$ .  $\psi$  is the precession of the shell with respect to the plane  $XOY$ .

$OABC$  is a system of rectangular axes, of which  $OA$  lies in the plane of yaw. Let  $C$  be the moment of inertia of the shell about its axis of spin  $OB$ . Let  $A$  be that about any transverse axis, since the shell is symmetrical about its axis

Fig. 2.



of spin. Let  $\omega$  be the spin of the projectile relatively to the moving plane  $AOB$ .

Then the motion of the projectile about its centre of gravity relatively to the system  $OXYZ$  is completely determined by  $\phi$ ,  $\psi$ , and  $\omega$ , these being precisely the same quantities as are commonly employed in the theory of the ordinary spinning-top, where the system  $OXYZ$  is fixed.

Let the total instantaneous angular velocities of the projectile about  $OB$ ,  $OA$ ,  $OC$  be respectively  $\Omega$ ,  $\Omega_1$ ,  $\Omega_2$ .

The system of axes  $OXYZ$  is determined in every position by the following convention:—

As the centre of gravity moves the plane  $XOY$  always contains  $OX'$ .

Let the direction cosines of  $OY$  with respect to  $OX'$ ,  $Y'$ ,  $Z'$  be  $l_2$ ,  $m_2$ ,  $n_2$ .

The general values of  $\dot{\xi}$ ,  $\dot{\eta}$ ,  $\dot{\zeta}$  are

$$\left. \begin{aligned} \dot{\xi} &= -\dot{\alpha} \cos \gamma - \dot{\theta} \sin \gamma \sin \alpha, \\ \dot{\eta} &= -\dot{\alpha} \sin \gamma + \dot{\theta} \cos \gamma \sin \alpha, \\ \dot{\zeta} &= \dot{\gamma} + \dot{\theta} \cos \alpha. \end{aligned} \right\} \quad . \quad . \quad . \quad (2)$$

*The Dynamical Equations.**The motion of the centre of gravity.*

The forces acting upon the centre of gravity are :—

- (1) The drag  $R$  acting along  $YO$  and directly opposed to the direction of motion.
- (2) A force  $F_1$  acting in the plane of yaw, perpendicularly to  $OY$ , and in the direction  $OA'$  (fig. 2).

Let  $m$  be the mass of the projectile, and  $v$  its velocity.

Let angle  $YOV = \beta$ .

Since the centre of gravity is moving along  $OY$  with velocity  $v$ ,

$$\begin{aligned} m \frac{\partial r}{\partial t} &= -R - mg \cos \beta \\ &= -R - mg [\cos \theta \sin \gamma + \sin \theta \cos \gamma \cos \alpha]. \end{aligned} \quad (3)$$

Since the motion in the directions  $OX'$  and  $OZ'$  is referred to axes rotating about  $OZ'$  with angular velocity  $\dot{\theta}$ , the equations of motion parallel to  $OX'$  and  $OZ'$  are respectively

$$m \left\{ \frac{\partial}{\partial t} (l_2 v) + m_2 v \dot{\theta} \right\} = -R l_2 - mg \cos \theta + F_1 \cos \psi \cos \gamma, \quad (4)$$

and

$$\begin{aligned} m \frac{\partial}{\partial t} (n_2 v) &= -R n_2 + F_1 \sin \psi \cos \alpha \\ &\quad - F_1 \cos \psi \sin \gamma \sin \alpha, \end{aligned} \quad (5)$$

$l_2, m_2, n_2$  being subsequently expressed in terms of  $\alpha$  and  $\gamma$ .

*The motion about the centre of gravity.*

The total kinetic energy of rotation is

$$T = \frac{1}{2} [C\Omega^2 + A(\Omega_1^2 + \Omega_2^2)], \quad (6)$$

in which, as can be readily verified,

$$\left. \begin{aligned} \Omega &= \omega + (\dot{\psi} + \dot{\eta}) \cos \phi + (\dot{\zeta} \sin \psi + \dot{\xi} \cos \psi) \sin \phi, \\ \Omega_1 &= (\dot{\psi} + \dot{\eta}) \sin \phi - (\dot{\zeta} \sin \psi + \dot{\xi} \cos \psi) \cos \phi, \\ \Omega_2 &= \dot{\phi} + \dot{\zeta} \cos \psi - \dot{\xi} \sin \psi. \end{aligned} \right\} \quad (7)$$

It is assumed that there are three couples  $M_0, M_1$ , and  $M_2$  acting about  $OB, OA$ , and  $OC$  respectively.

Lagrange's equations are extremely complicated, when

expanded, but the following equivalent equations are concise and convenient:—

$$\left. \begin{aligned} C \frac{\partial \Omega}{\partial t} &= M_0, \\ \frac{1}{\sin \phi} \left[ A \sin \phi \frac{\partial \Omega_1}{\partial t} - (C \Omega \sin \phi - A \Omega_1 \cos \phi) \Omega_2 + A \Omega_2 \frac{\partial \Omega_2}{\partial \psi} \right] &= M_1, \\ A \frac{\partial \Omega_2}{\partial t} + C \Omega \Omega_1 - A \Omega_1 \frac{\partial \Omega_1}{\partial \phi} &= M_2, \end{aligned} \right\} \quad (8)$$

in which the differential coefficients with respect to  $\phi$  and  $\psi$  are partial.

### *The Initial Motion.*

In considering the initial motion of a shell  $\phi$  may be taken as small.  $\xi$ ,  $\zeta$ , and  $\theta$  are also small, so that the squares and products of all these quantities may be neglected.

In Section 2 the values of  $M_0$ ,  $M_1$ ,  $M_2$ ,  $F_1$  are given. The following abbreviations are convenient:—

$$\left. \begin{aligned} \frac{C\Omega}{A} &= P & \frac{F'}{mr} &= F \\ \phi e^{i\psi} &= u & -\ddot{\theta} + iP\dot{\theta} - L\dot{\theta} &= iPH \\ Q &= \zeta - i\xi & \frac{N'}{A} &= N \\ & & \frac{L'}{A} &= L \\ & & \frac{M'}{A} &= M_1. \end{aligned} \right\} \quad (9)$$

The last two equations of (8) then combine into the complex equation

$$\frac{\partial^2}{\partial t^2}(u + Q) - (iP - L) \frac{\partial}{\partial t}(u + Q) - (M_1 + iN)u = iPH, \quad (10)$$

and the equations of motion of the centre of gravity combine into

$$\frac{\partial}{\partial t} \left( \frac{Q}{\cos \theta} \right) = \frac{Fu}{\cos \theta} \dots \dots \dots (11)$$

Equations (10) and (11) determine the whole motion, when  $\phi$  is small.

The motion of the centre of gravity is given by the formula

$$Q = \frac{\dot{x} + i\dot{z}}{r} \dots \dots \dots (12)$$

## Section 2.—THE FORCE SYSTEM.

As mentioned in the introduction, the forces acting upon the shell take remarkably simple forms when the velocity exceeds 1000 f.s. In this section the force system will be formulated in accordance with this observation.

An interesting paper by Mallock upon "Air Resistance" appeared in the Royal Soc. Proc. vol. lxxix., and was followed in the same volume by a paper upon "The Ranges and Behaviour of Rifled Projectiles in Air."

In the latter paper he applies a very simple law of resistance in the discussion of the motion of a shell with a very flat trajectory.

This law of resistance applies to projectiles moving with speeds varying from about the velocity of sound to above three times that velocity.

The most important force acting through the centre of gravity is the "drag," and it is remarkable that the resistance curve for pointed projectiles, where resistance is plotted against velocities ranging from about 1000 f.s. to 3000 f.s., is almost a straight line cutting the abscissa at the point representing 850 f.s. and the 3000 f.s. ordinate at the point representing 40 lb. per square inch of the cross section of the shell.

Let  $V_0$  = the muzzle velocity of the shell.

$r$  = the velocity of the shell at any instant.

$u_0$  = 850 f.s.

$W$  = weight of shell in lb.

$m$  = mass of shell.

$R$  = drag.

$f$  = retardation of shell.

$d$  = diameter of shell in inches.

$R'$  = resistance in lb. per square foot of cross-sectional area of the shell.

It is found that the resistance is given by the equation

$$\left. \begin{array}{l} \text{Let} \\ \text{Then} \\ \text{and} \end{array} \right\} \begin{array}{l} R' = 2.53 (V - u_0). \\ \lambda = \frac{2.53 \pi d^2 g}{4 \times 144 \cdot W}. \\ R = mf = \frac{W}{g} f, \\ f = \lambda (r - u_0). \end{array} \quad \dots \dots (13)$$



This simple equation for the retardation represents the motion very accurately.

When the velocity of the shell exceeds that of sound, the forces and couples may be expressed very approximately as follows :—

- (1) A couple  $M_2$  tending to increase  $\phi$ .

$$M_2 = \left[ \frac{\kappa}{m\lambda} R + \kappa(u_0 - u_1) \right] \sin \phi,$$

where  $u_1$  is a constant depending upon the nature of the shell, and  $u_0 - u_1$  is small.

This couple is important in the production of drift.

Write

$$M_2 = M' \sin \phi.$$

- (2) A force  $F_1$  acting along  $OA'$  through the centre of gravity and in the plane of yaw.

$$F_1 = \frac{\kappa' M v}{v_0 - u_0} \sin \phi,$$

where  $\kappa'$  is a constant depending upon the form of the shell.

Write

$$F_1 = F' \sin \phi.$$

- (3) A couple  $M_1$  acting about  $OA$ , tending to increase the rate of precession.

This couple is small compared with  $M_2$  but it has an important effect upon the stability of the shell.

Write

$$M_1 = N' \sin \phi.$$

- (4) A couple tending to retard both the increase of  $\phi$  and the rate of precession. This couple has two components proportional to  $\Omega_1$  and  $\Omega_2$  respectively. These components will be written  $L'\Omega_1$  and  $L'\Omega_2$ , the coefficient  $L'$  being the same in both owing to the symmetry of the shell about its axis.

- (5) The air-friction couple tending to reduce the spin can be neglected over the initial portion of the trajectory.

Until the velocity of the shell drops to about that of sound the above relations connecting the forces, which act upon the shell, have been shown by experiment on a particular form of shell to be the true relations with a considerable degree of certainty.

Experiment appears to show that the shell settles down to a motion in accordance with theory in a small fraction of a second after it leaves the muzzle of the gun. It is, therefore, highly probable that the following theory gives a very accurate picture of the complete motion of the shell at all

angles of fire during a period of its time of flight equal to seven or eight seconds. Beyond this time in high angle fire the curvature of the trajectory begins to become effective in modifying the motion of the shell. Furthermore, the force system ceases to obey the above laws. A step by step method for the integration of the equations of motion has then to be adopted.

In the case, however, of high velocity shells and low trajectories, which are common in naval gun-fire, the theory presents a very complete solution. For in these cases the force system is valid throughout the whole time of flight.

In order to establish the simple law of resistance in high angle fire a short discussion is given of the initial portion of the plane trajectory for the 3 inch 20 cwt. anti-aircraft gun, firing a 16 lb. shell. In this case

$$V_0 = 2000 \text{ f.s.}$$

$$\lambda = \frac{1}{4}.$$

### *The Plane Trajectory.*

*The Equations of the trajectory under the law of retardation,*  
 $f = \lambda(r - u_0).$

It is assumed that the axis of the projectile is always very nearly in the direction of the tangent to the trajectory.

The resistance of the air is therefore effectively tangent to the trajectory.

Then for the equations of motion we have

$$\left. \begin{aligned} \ddot{x} &= -\lambda(r - u_0) \cos \theta, \\ \ddot{y} &= -g - \lambda(r - u_0) \sin \theta, \end{aligned} \right\} \quad \dots \quad (14)$$

where  $\theta$  is the angle which the tangent to the trajectory makes with the horizontal.

Now in the applications of the theory the departure of  $\theta$  from its initial value  $\theta_0$  is never very great. It is, therefore, tentatively assumed that throughout the flight

$$\left. \begin{aligned} u_0 \cos \theta &= u_0 \cos \theta_0, \\ \text{and } u_0 \sin \theta &= u_0 \sin \theta_0, \end{aligned} \right\} \quad \dots \quad (15)$$

Integration of (14) gives

$$\left. \begin{aligned} x &= u_0 \cos \theta_0 \cdot t + \frac{1}{\lambda} (r_0 - u_0) \cos \theta_0 (1 - e^{-\lambda t}), \\ y &= \left( u_0 \sin \theta_0 - \frac{g}{\lambda} \right) t + \frac{1}{\lambda} \left[ (r_0 - u_0) \sin \theta_0 + \frac{g}{\lambda} \right] (1 - e^{-\lambda t}). \end{aligned} \right\} \quad (16)$$

In applying the theory to the results of observation, for

any given trajectory, the maximum time of flight is required throughout which the theory is valid. This is given approximately by

$$v_0 e^{-\lambda t} + u_0 = \frac{g}{\lambda} \sin \theta_0 \pm u_0.$$

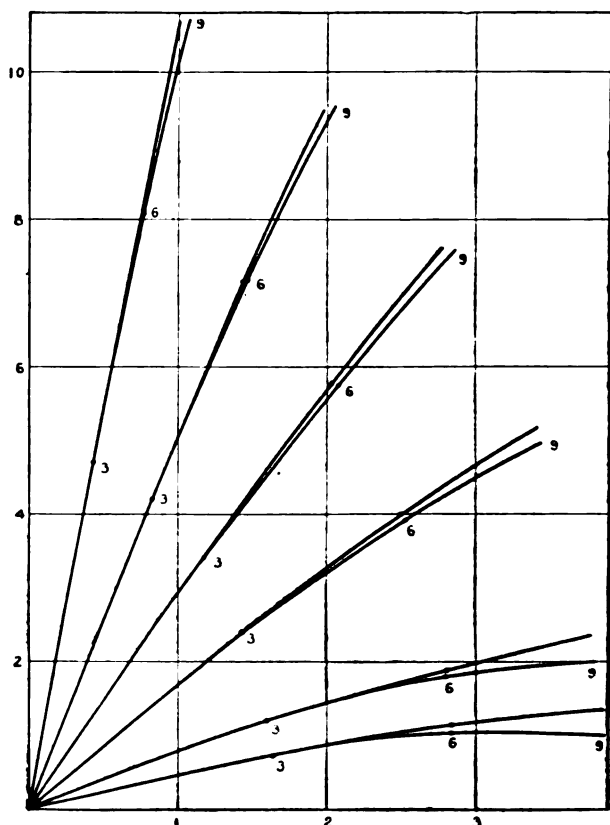
Since  $u_0$  is considerably greater than  $\frac{g}{\lambda} \sin \theta_0$ , the positive sign on the right hand is alone admissible.

Hence

$$e^{-\lambda t} = \frac{g \sin \theta_0}{\lambda v_0} \dots \dots \dots (17)$$

The actual maximum times permissible must be somewhat less than those given by (17).

Fig. 3.



In fig. 3 are shown the initial portions of the trajectories for angles of quadrant elevation  $10^\circ$ ,  $15^\circ$ ,  $30^\circ$ ,  $45^\circ$ ,  $60^\circ$ , and  $75^\circ$ .

Horizontal abscissæ represent thousands of yards. Vertical ordinates represent thousands of feet. The upper curve in each case is that calculated by means of equations (16). The lower curve is that obtained by more accurate methods involving a combination of theory and observation. The figures on the curves represent the times of flight.

It may be remarked that, in so far as distance travelled is concerned, the differences between the curves are small. Discrepancies in other respects are to be expected. For, in the first place, the solution is an approximation owing to the assumptions (15). In the second place, no account has been taken, in applying the simple law, of the decrease in the density of the air at high altitudes. It is, however, unexpected that the agreement is so close as it is in the case of the  $75^\circ$  trajectory.

There would seem to be no doubt, however, that, during the first few seconds after the shell leaves the muzzle of the gun, Maillock's law of retardation may be used to study the effect of the diminishing precessional couple upon the oscillations of the shell.

### Section 3.—THE SOLUTION OF THE EQUATIONS.

In the equation (10) write

$$M_1 + iN = K. \quad . \quad . \quad . \quad (18)$$

Now  $H$  is a function of  $\theta$  only, and is known in terms of the time. Hence the solution of (10) consists of a complementary function and a particular integral.

An approximation to the complementary function was obtained by Horn and Schlesinger (see 'Aerodynamics of a Spinning Shell') by making the substitutions

$$u = e^{iP\tau} u_1, \\ Q = e^{iP\tau} Q_1,$$

and treating  $u_1$  and  $Q_1$  as constants.

Making these substitutions it is found that, retaining only the highest power of  $P$ ,

$$\ddot{x} \left( \dot{x}^2 - \dot{x} + \frac{K}{P^2} \right) = 0. \quad . \quad . \quad . \quad (19)$$

This is sufficient to show that, with an error of the order  $1/P$ , the solution of (10) may be obtained by omitting  $Q$  altogether.

A first approximation to the particular integral is then given by

$$\frac{\partial u}{\partial t} + \frac{K}{iP} u = -H,$$

or

$$u e^{\frac{K}{iP}t} = - \int H e^{\frac{K}{iP}t} \partial t.$$

If  $s$  stand for the stability factor  $\frac{P^2}{4L}$ , the approximation required is

$$u = - \frac{4isH}{P}.$$

If  $\dot{\theta}$  is taken as constant and  $\ddot{\theta}$  neglected, the particular integral in the solution for  $u$  is a small quantity of order  $1/P$  which slowly increases. Since  $\dot{\theta}$  is always extremely small, over the initial path, compared with  $P$ , the particular integral may be neglected throughout.

It is permissible, therefore, to neglect the variation of  $\theta$  over the initial path. Since  $F$  is small, it will be treated as constant.

Equation (10) with the help of (11) reduces to

$$\frac{\partial^2 u}{\partial t^2} - i(P + iL + iF) \frac{\partial u}{\partial t} - (M_1 + iN + iPF - LF)u = 0. \quad (20)$$

The solution of this equation is identical with that of a spinning top under a special system of impressed forces.

To solve (20), let

$$u = w e^{(i\frac{P}{2} - \frac{L+F}{2})t}.$$

Then

$$\frac{\partial^2 w}{\partial t^2} + w \{R^2 - M_1\} = 0, \quad . \quad . \quad . \quad (21)$$

where

$$R = \frac{P}{2} + \frac{i(L-F)}{2} - \frac{iN}{P},$$

very approximately. All the terms of highest order in the damping forces  $L$ ,  $F$ , and  $N$  have been retained. While real quantities which are small compared with  $P$  have been neglected.

It appears in the discussion of the force system that

$$M_1 = M e^{-\lambda t} \quad \text{approximately,}$$

the approximation again consisting in the neglect of a real quantity which is small compared with  $P$ .

Equation (21) can be solved in series, the complete solution being

$$w = A_1 e^{iRt} \left[ 1 + \frac{M}{m_2^2 + R^2} e^{-\lambda t} + \frac{M^2}{(m_2^2 + R^2)(m_3^2 + R^2)} e^{-2\lambda t} + \dots \right] \\ + B_1 e^{-iRt} \left[ 1 + \frac{M}{n_2^2 + R^2} e^{-\lambda t} + \dots \dots \dots \right]. \quad (22)$$

The general term of the first series in square brackets may be written in the form

$$\frac{(ix)^n}{n(1+i\mu)(1+2i\mu)\dots(1+ni\mu)}.$$

That of the second series in the form

$$\frac{(-1)^n(ix)^n}{n(1-i\mu)\dots\dots\dots(1-ni\mu)}.$$

The moduli of the coefficients of  $\frac{x^n}{n}$  in these terms are less than unity. Hence each series is less than the exponential series  $e^x$ . The series are, therefore, convergent for all finite values of  $x$ .

With regard to the periodicity of the solution the following theorem may be proved:—

Let  $w$  satisfy the equation

$$\frac{\partial^2 w}{\partial t^2} + wF = 0, \quad \dots \dots \dots (23)$$

where  $F$  is a function of  $t$  which remains positive throughout the motion. Then  $w$  must have an infinite number of real roots. This is true if  $F$  is constant but requires formal proof if  $F$  is variable. Differentiate (23)  $n$  times, then  $(n-1)$  times, and so on. Then

$$\left[ \frac{D^{n+2}w}{D^n w} + F \right] D^n w + \dots \dots \dots + w D^n F = 0, \\ \left[ \frac{D^{n+1}w}{D^n w} \right] D^n w + D^{n-1}w \cdot F + \dots \dots \dots + w D^{n-1}F = 0, \\ D^n w + 0 + D^{n-2}w \cdot F + \dots + w D^{n-2}F = 0, \\ \dots \dots \dots \\ 0 + \dots \dots \dots + D^2 w + w \cdot F = 0.$$

On eliminating  $D^n w, \dots, w$  from these  $n$  equations,

$$[D^{n+2}w + D^n w \cdot F] F_1 + D^{n+1}w \cdot F_2 = 0,$$

where  $F_1$  and  $F_2$  are functions of  $t$ .

Since  $F$  is always positive, the reality of the roots is established by Fourier's rule.

Now

$$\begin{aligned}\mu &= \frac{\lambda}{2R} \\ &= \frac{\lambda}{P + i(L - F) - \frac{2iN}{P}},\end{aligned}$$

giving as a first approximation to the value of  $\mu$

$$\mu = \frac{\lambda}{P}.$$

In practice  $x$  never becomes very large, so that a sufficient approximation can be obtained by taking a number of terms of each series for which  $n$  is not very large.

In the case of the 3-inch shell  $\lambda = .25$ , and  $P = 157$ , which give for the approximate value of  $\mu$ :

$$\begin{aligned}\mu &= \frac{\lambda}{P} \\ &= .0015. \dots \dots \dots (24)\end{aligned}$$

Consider now the coefficient

$$R_n = \frac{1}{(1 + i\mu) \dots (1 + ni\mu)}.$$

$$\begin{aligned}\log R_n &= -\int \partial \mu \left[ \frac{i}{1 + i\mu} + \frac{2i}{1 + 2i\mu} + \dots + \frac{ni}{1 + ni\mu} \right] \\ &= -i \sum_1^n \tan^{-1}(n\mu) + \log \{ (1 + \mu^2) \dots (1 + n^2\mu^2) \}^{-\frac{1}{2}}.\end{aligned}$$

Hence

$$\begin{aligned}R_n &= \{ (1 + \mu^2) \dots (1 + n^2\mu^2) \}^{-\frac{1}{2}} \{ \cos \sum_1^n \tan^{-1}(n\mu) \\ &\quad - i \sin \sum_1^n \tan^{-1}(n\mu) \}.\end{aligned}$$

With regard to  $x$ , a first approximation, neglecting terms of the order  $1/P^3$ , gives

$$x = \frac{M e^{-\lambda t}}{P \lambda}.$$

The coefficients  $R_n$  are very involved. It is, therefore, necessary to consider their magnitude.

Since  $\mu$  is very small the coefficients  $R_n$  are nearly equal to unity unless  $x$  is so large that a very considerable number of terms of the series requires to be taken. Now very much the most important part of  $x$  is  $Me^{-\lambda t}/P\lambda$ , the other parts being negligible in comparison. At the beginning of the motion the value of  $x$  is approximately 12, but after three seconds it drops to about 5.

It is necessary to investigate the nature of the error involved in assuming that each coefficient  $R_n$  is equal to unity.

The only term in  $R_n$  requiring consideration is  $n^2\mu$ , such terms as  $n\mu$ ,  $n^3\mu^2$ , etc., being small in comparison up to the values of  $n$  which are required. In  $R_n$ , therefore, consider the term

$$-i\mu \{1+2+\dots+n\} \quad \text{or} \quad -i\mu \frac{n(n+1)}{2}.$$

The series

$$-i \sum_1^\infty \frac{(ix)^n}{n!} \frac{n(n+1)}{2} \mu,$$

since such terms as  $n\mu$  may be neglected, may be written

$$x\mu - i \sum_2^\infty \frac{(ix)^n}{n!} \frac{n(n-1)}{2} \mu,$$

$$\text{or} \quad \frac{i\mu x^2}{2} \sum_2^\infty \frac{(ix)^{n-2}}{n-2},$$

$$\text{or} \quad \frac{i\mu x^2}{2} e^{ix}. \quad \dots \quad (25)$$

$\frac{\mu x^2}{2}$  is therefore the error involved, since  $e^{ix}$  is the value of the first series when the coefficients  $R_n$  are taken as unity. The error involved in the second series is  $-\frac{1}{2}\mu x^2$ .

In the beginning of the motion this error amounts to about 10 per cent., but after three seconds it drops to about 4 per cent. This is an error in the value of the yaw and the precession of the shell, but, considering the uncertainties of the initial motion of the shell and especially the very small value of the yaw, it is unnecessary to take it into account. It is sufficient to know its approximate magnitude.



It is easy to verify (25). For, writing  $w = Ae^r$ , we have

$$\frac{\partial^2 r}{\partial t^2} + \left(\frac{\partial r}{\partial t}\right)^2 + R^2 - Me^{-\lambda t} = 0. \quad (26)$$

This equation, not being linear, is not adapted to general solution in series, but can be used to obtain an approximate solution.

Let

$$r = a_0 t + a_1 e^{-\lambda t} + a_2 e^{-2\lambda t} + \dots$$

On substitution in (26) it is found that

$$a_0 = \pm iR,$$

$$a_1 e^{-\lambda t} = \pm ix,$$

$$a_2 e^{-2\lambda t} = \pm \frac{i\mu x^2}{2}.$$

Hence

$$w = A_1 e^{iRt + ix} \left[ 1 + \frac{i\mu x^2}{2} \right] + B_1 e^{-iRt - ix} \left[ 1 - \frac{i\mu x^2}{2} \right] \quad \text{approx.}$$

The coefficients  $R_n$  will now be put equal to unity, and the value of  $x$  equal to  $Me^{-\lambda t}/P\lambda$ .

Let

$$\rho = \frac{P}{2}t - \frac{M}{P}u,$$

$$\text{where} \quad u = \frac{1}{\lambda}(1 - e^{-\lambda t}).$$

Let

$$\sigma = -L + \frac{N}{P}$$

$$\text{and} \quad \tau = -F - \frac{N}{P}.$$

Then it can be shown that

$$\phi e^{i(\psi - \frac{P}{2}t)} = A e^{i(\rho + \alpha)} e^{\sigma t} + B e^{-i(\rho + \beta)} e^{\tau t}, \quad (27)$$

where  $A, B, \alpha, \beta$  are real constants to be determined by the initial conditions. On differentiating (27) with respect to  $t$ ,

$$\begin{aligned} \left\{ \phi + i\phi \left( \dot{\psi} - \frac{P}{2} \right) \right\} e^{i(\psi - \frac{P}{2}t)} \\ = A(\sigma + i\dot{\rho}) e^{i(\rho + \alpha)} e^{\sigma t} + B(\tau - i\dot{\rho}) e^{-i(\rho + \beta)} e^{\tau t}, \quad (28) \end{aligned}$$

which can be simplified since  $\sigma$  and  $\tau$  are extremely small compared with  $\dot{\rho}$ .

For the initial conditions take a maximum value of  $\phi$ , occurring in the rapid oscillations set up when the shell leaves the muzzle of the gun. In this case  $\dot{\phi}$  is initially zero.

Let  $\psi$  be measured from the plane of initial maximum yaw.

Then initially,

$$\phi = \phi_0,$$

$$\psi = 0,$$

$$\dot{\phi} = 0,$$

$$\dot{\psi} = \dot{\psi}_0.$$

Let

$$\frac{\frac{P}{2} - \dot{\psi}_0}{\frac{P}{2} - \frac{M}{P}} = \kappa = \tanh \mu. \quad . \quad . \quad . \quad (29)$$

These initial conditions are satisfied if

$$\alpha = \beta = 0,$$

$$\phi_0 = A + B,$$

$$-\kappa \phi_0 = A - B.$$

Hence

$$A = (1 - \kappa) \frac{\phi_0}{2},$$

$$B = (1 + \kappa) \frac{\phi_0}{2}.$$

Then from (27)

$$\tan\left(\psi - \frac{P}{2} t\right) = \frac{M}{N} \tan \rho = K \tan \rho \quad (\text{say}).$$

The limiting circles between which  $\phi$  oscillates are given by

$$M \frac{\phi_0}{2} \quad \text{and} \quad N \frac{\phi_0}{2},$$

$$\text{where} \quad M = (1 - \kappa) e^{\sigma t} - (1 + \kappa) e^{\tau t}$$

$$\text{and} \quad N = (1 - \kappa) e^{\sigma t} + (1 + \kappa) e^{\tau t}.$$

Let

$$-\chi = \frac{\sigma}{2} + \frac{\tau}{2}$$

and

$$-\nu = \frac{\sigma}{2} - \frac{\tau}{2}.$$

Then

$$\left. \begin{aligned} M &= -2e^{-\lambda t} \operatorname{sech} \mu \sinh (vt + \mu), \\ N &= 2e^{-\lambda t} \operatorname{sech} \mu \cosh (vt + \mu). \end{aligned} \right\}$$

These give

$$\tan\left(\psi - \frac{P}{2}t\right) = -\tanh(vt + \mu) \tan \rho. \quad (30)$$

These equations represent the whole motion, with

$$\begin{aligned} \chi &= \frac{L+F}{2}, \\ \nu &= \frac{L-F}{2} - \frac{N}{P}. \end{aligned}$$

From (30), by differentiation,

$$\dot{\psi} - \frac{P}{2} = K\dot{\rho} \frac{1 + \tan^2 \rho}{1 + K^2 \tan^2 \rho} + \dot{K} \frac{\tan \rho}{1 + K^2 \tan^2 \rho}. \quad (31)$$

With the help of these equations it is possible to discuss very completely the motion of the projectile. It is found that it depends greatly upon the initial value of the precession  $\dot{\psi}_0$ .

Case I.—Let  $\dot{\psi}_0 = \frac{M}{P}$ , i. e. let  $\kappa = 1$ , or  $\mu = \infty$ .

This would be the ordinary slow precession if the forces were constant.

Then  $K=1$ , nearly, throughout the motion. Also  $\dot{K}=0$ . From (31)

$$\begin{aligned} \dot{\psi} - \frac{P}{2} &= -\rho \\ &= -\frac{P}{2} + \frac{M}{P} e^{-\lambda t}. \end{aligned}$$

Hence

$$\dot{\psi} = \frac{M}{P} e^{-\lambda t}.$$

The limiting circles of maximum and minimum yaw are nearly coincident throughout the motion and

$$\phi = \phi_0 e^{-\lambda t}. \quad (32)$$

Hence the angle of yaw and the rate of precession decrease continually. The motion is completely stable.

Case II.—Consider now the case when  $\dot{\psi}_0$  is greater than  $\frac{M}{P}$  but less than  $\frac{P}{2}$ .

Then  $\kappa < 1$  and positive.

The initial values of the limiting circles are  $\phi_0$  and  $\kappa\phi_0$ .

It is interesting to interpret the motion of the axis of the projectile between its limiting circles.

For this purpose employ equation (31). During a very short interval of time, comprising, however, a number of the very small periods  $\frac{\pi}{P}$ ,  $\dot{K}$  may be treated as sensibly constant.

Initially  $K$  is negative and remains always negative.

During the short interval, the beginning of which will be taken as origin of time,  $\dot{\rho}$  may be considered constant.

The following sequence is obtained :—

$$\left. \begin{array}{ll} \text{When } t = 0 & \dot{\psi} - \frac{P}{2} = K\dot{\rho}, \\ \text{,, } t = \frac{\pi}{4\dot{\rho}} & \text{,, } = \frac{2K\dot{\rho}}{1+K^2} + \frac{\dot{K}}{1+K^2}, \\ \text{,, } t = \frac{\pi}{2\dot{\rho}} & \text{,, } = \frac{K\dot{\rho}}{K^2}, \\ \text{,, } t = \frac{3\pi}{4\dot{\rho}} & \text{,, } = \frac{2K\dot{\rho}}{1+K^2} - \frac{\dot{K}}{1+K^2}, \\ \text{,, } t = \frac{\pi}{\dot{\rho}} & \text{,, } = K\dot{\rho}. \end{array} \right\}$$

It is seen that the only effect of  $\dot{K}$  on the oscillations is to slightly modify the path of the axis from one limiting circle to the other.

During the period  $\frac{\pi}{\dot{\rho}}$ ,

$$\tan\left(\dot{\psi} - \frac{P}{2}t\right) = K \tan \dot{\rho}t.$$

By the end of this period  $\dot{\psi}$  has increased by an amount

$$\begin{aligned} \dot{\psi}_1 &= \frac{P}{2} \frac{\pi}{\dot{\rho}} - \pi \\ &= 2\pi M e^{-\lambda t} \quad \text{approx.} \end{aligned}$$

Hence

$$\dot{\psi}_1 = \frac{M}{P} e^{-\lambda t}, \quad \text{approximately.}$$

If C be the point of contact of the path of the axis with the outer circle, say, then  $\dot{\psi}_1$  is the velocity of this point of contact.

It is not difficult, now, to understand the course of the projectile's axis. It is probable that, at the instant of leaving the muzzle of the gun, the motion of the projectile is extremely unsteady. But, at a very short distance from the muzzle, the projectile settles down to a stable gyroscopic motion, with its axis nearly tangential to the trajectory. The case of  $K=1$ , which corresponds to  $\kappa=1$ , has been discussed.

If  $\kappa < 1$ ,  $K$  is initially less than 1 and negative.  $\dot{\psi}$  then becomes zero in the passage of the axis from the outer to the inner circle, and again on the passage back to the outer circle.

Hence there are loops in the path, the nodes occurring near the outer circle. As  $K$  increases in absolute value with time, the nodes in the path approach the inner circle.

As  $K$  approaches the value  $-1$  with increase in  $t$ ,  $\dot{\psi}$  settles down to a slow precessional value.

*Case III.*—If  $\kappa$  and therefore  $\mu$  are negative, but  $|\kappa| < 1$ , then  $K$  is initially positive. In this case  $\dot{\psi}$  may not become zero during several of the periods  $\pi/\dot{\rho}$ , in which case the nose of the projectile precesses right round its direction of motion with a rapid precession. But with increase of time  $K$  becomes negative and the course of the axis follows that described in Case II. Here also  $\dot{\psi}$  settles down to the slow precession. The above theory, upon comparison with experiment, shows definitely that  $\nu$  is positive.

Consider now the theory of the limiting circles of yaw. With increase of time they approach one another and take the common value

$$e^{-(\chi-\nu)t} = e^{-(F+\frac{N}{P})t}.$$

Hence if  $F + \frac{N}{P}$  is positive the motion is always stable.

If  $\chi=0$  it is seen, from (32), that if the shell start off with the proper precession the yaw remains constant. But for any other value of the initial precession the motion is unstable.

If  $\chi$  is zero and  $\beta$  negative while  $\nu$  is positive, both circles decrease for a time  $t = \frac{\mu}{\nu}$ . At this time the inner

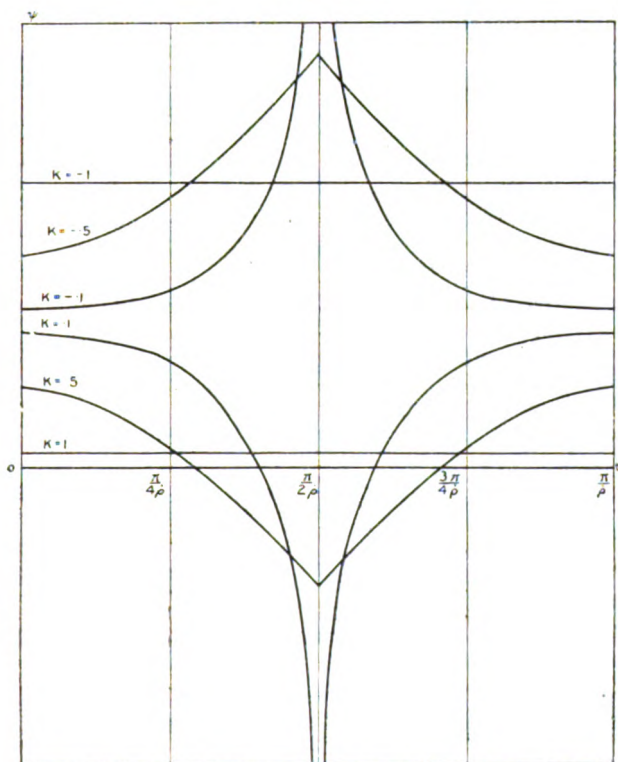
circle becomes zero and the outer a minimum. Thereafter both circles increase.

A motion in which the yaw initially decreases does not necessarily imply that the motion is subsequently stable.

The coefficient  $L$  always has a damping and therefore stabilising effect.  $F$  is shown by the theory and observations of drift to be positive, and therefore also has a stabilising effect.

In fig. 4 is shown the variation of  $\dot{\psi}$  for different values

Fig. 4.



of  $K$ . The figure is not intended to be exactly to scale, and for simplicity  $2\rho$  has been put equal to  $P - 1P$ , i. e., to  $\cdot 9P$ . The values of  $K$  taken are

$$1, \cdot 5, \cdot 1, -\cdot 1, -\cdot 5, -1.$$

For each value of  $K$ ,  $\dot{\psi}$  is plotted throughout the period  $\frac{\pi}{\rho}$ ,

which is the time of passage of the axis of the projectile from the outer circle to the inner and back to the outer.  $K$  is assumed to be constant throughout this small interval.

With regard to the particular integral, it is quite negligible till  $\dot{\theta}$  becomes large, but it then becomes important for both  $s$  (the stability factor) and  $\dot{\theta}$  are then large. It has been suggested that some means should be adopted to decrease the spin more rapidly and thus reduce  $s$ , so as to lessen this disturbing factor at the apex of a trajectory.

For initial elevations up to as much as  $45^\circ$  or  $50^\circ$  the effect of the trajectory on the yaw is negligible. The explanation of this important fact has only recently been given and is worthy of a simple explanation in words.

We have the well-known results in the theory of the spinning-top: if the precession is hurried the top rises; if it is retarded the top sinks. Now the projectile, neglecting the motion of its centre of gravity, is like a top spinning upon its point. The centre of gravity of the projectile corresponds to the point of the top. The air-pressure acting through the centre of pressure corresponds to gravity acting upon the top. In the case of the top, if the gravity couple were increased, the precession would be hurried and the top would rise. Now the curvature of the path, when the projectile's axis is pointing above the tangent, tends to increase the pressure-couple. Hence the precession is hurried and the nose of the projectile is lowered. When its axis is pointing below the tangent, the curvature of the path tends to decrease the pressure-couple. Hence the precession is retarded and the nose of the projectile is lowered still further.

It will be noted that the oscillations of the axis of the projectile are referred to the direction of motion of the centre of gravity of the projectile. There should, therefore, be added the helical oscillations of the latter in order to obtain the resultant oscillations relatively to the plane trajectory. It has, however, been shown that the angular helical oscillations of the centre of gravity are, so far as their most important periodic term is concerned, only a very small fraction of  $\phi$ , the yaw of the shell referred to the direction of motion of the centre of gravity. It is, accordingly, quite unnecessary to take them into account in questions connected with the stability of the projectile.

CXI. *An Experimental Determination of the Inertia of a Sphere Vibrating in a Liquid.* By N. C. KRISHNAIYAR, M.A., Lecturer in Physics, University College, Rangoon\*.

SIR G. G. STOKES † has shown analytically that in the case of a sphere attached to a fine wire of which the effect is neglected, and swung in an unconfined mass of incompressible liquid, the force exerted on the sphere by the motion of the surrounding liquid is given by the relation

$$F = -A \frac{d^2 y}{dt^2} - B \frac{dy}{dt},$$

where  $y$  is the displacement and  $t$  is the time and the coefficients  $A$  and  $B$  have the following values,

$$A = \left(\frac{1}{2} + 9/4\lambda r\right)M'; \quad B = (9/4\lambda r) \left(1 + \frac{1}{\lambda r}\right)M'a,$$

where  $M'$  is the mass of the fluid displaced by the sphere,  $r$  is the radius,  $a = 2\pi/T$  where  $T$  is the period of oscillation, and  $\lambda = (a/2\mu')^{1/2}$  and  $\mu'$  = coefficient of viscosity  $\div$  density. The first term in the expression for the force  $F$  has the same effect as increasing the inertia of the sphere. To take this term into account it will be sufficient to conceive a mass  $M$  collected at the centre of the sphere, adding to its inertia without adding to its weight. The second term gives a frictional force varying as the velocity, and the effect is mainly to produce diminution in the arc of oscillation. The assumptions made were that the centre of the sphere performed small periodic oscillations along a straight line, that the sphere had a motion of translation only, that the velocities were so small that their squares could be neglected, and that there was no slipping of the fluid along the surface of the solid in contact with it. The application of the theory to the pendulum observations of Bessel and Baily was very satisfactory in the case of pendulums swinging in the air; but in the case of pendulums swinging in water or a more viscous liquid, conclusive results were not possible on account of the rapid diminution of the arc of oscillation.

G. F. McEwen ‡ measured the force acting on a sphere swinging in water and in a very viscous oil by employing a forced vibration method in which the sphere was suspended

\* Communicated by the Author.

† 'Cambridge Philosophical Transactions,' 1850; 'Collected Papers,' vol. iii, p. 34. The same result has been obtained by a different method. Lamb's 'Hydrodynamics,' 3rd ed., p. 584.

‡ Phys. Rev., 5th ser. vol. xxxiii. pp. 492-511 (1911).



by a fine wire, and had a slow motion of translation only along a vertical line. The oscillations were small, and either diminished very slowly or were maintained constant for any desired length of time. The forcing was done by a mechanical arrangement and a satisfactory measurement of the force was obtained. H. T. Barnes\*, by an arrangement in which a spherical pendulum bob moving under water was received by a ballistic pendulum, found that its effective inertia comes from the addition to its own mass of half the mass of the liquid that would fill the space occupied by the sphere. Gilbert Cook† determined the inertia of a large spherical mine-case falling freely through water under the influence of gravity. The theoretical increase of inertia in such cases is  $\frac{1}{2}$  the mass of the displaced liquid, and Gilbert Cook obtained the value 0.46.

In the present paper is described an arrangement in which the inertia of bodies vibrating with constant frequency inside a liquid can be determined under conditions which approximate, to a large extent, to the assumptions made in the hydrodynamical theory. The author has found that thin wires can be maintained in steady transverse vibration if they carry a small direct current and are placed between the poles of an electromagnet actuated by a single-phase alternating current, if the length and tension of the wires are adjusted to give the same natural frequency as the number of cycles of the alternating current. With the same current and the same length of wire the range of tension for the vibration to be maintained is limited, and the tension for resonance can be found from that which gives the maximum amplitude. If a small mass  $m$  be at the middle point of a wire of length  $l$  and mass per unit length  $\sigma$ , and if  $m$  be large in comparison with  $\sigma l$ , the tension required to give the system a natural frequency  $n$  is given by the relation ‡

$$T = \pi^2 n^2 / m \left( 1 + \frac{\sigma l}{6m} \right)^3.$$

If the tension is applied by hanging a mass  $M$  from the free end of the wire passed over a light pulley,  $T = Mg$ . If  $T_1$  and  $T_2$  be the values of the tension for best resonance, determined experimentally, when the system is in air and when it is immersed in a large mass of a liquid, and if  $m_1$

\* 'Transactions of the Royal Society of Canada,' vol. xi. June-Sept. 1917.

† Phil. Mag. vol. xxxix. (1920).

‡ Rayleigh's 'Sound,' vol. i. art. 136.

and  $m_1 + km_2$  be the inertia of the body in air and in the liquid,

$$\frac{T_1}{T_2} = \frac{m_1 + km_2}{m_1} \left\{ \frac{1 + \frac{(\sigma l)}{6(m_1 + km_2)}}{1 + \frac{\sigma l}{6m_1}} \right\}^2,$$

where  $m_2$  is the mass of the liquid displaced by the body and  $k$  is the inertia factor of the body in the liquid. The wire also increases in inertia when in the liquid. In the experiments the mass of the wire  $\sigma l$  is small in comparison with the mass of the body, and the increase is allowed for by making use of Stokes's table \* for cylinders vibrating transversely. Moreover, the quantities  $\sigma l$  and  $m_1$  were so chosen that when Stokes's theory was applied the quantity within the bracket was very nearly equal to unity. The frequency  $n$  of the maintained vibration does not enter the final formula, and all that is necessary is the frequency of the alternating current should be steady during the experiment.

A silver-plated steel wire of radius 0.009 cm., fixed at one end, passed horizontally under two sharp edges 30 cm. apart, and then over a fixed light aluminium pulley with ball bearings. Weights could be added to a pan attached to the free end of the wire. The fixed point and the top of the pulley were slightly higher than the level of the edges, so that the wire was well pressed against the edges. Spheres were fixed with gelatine-glycerine cement in the middle of the wire between the wedges. Near the two edges, on either side of the wire parallel to its length, were the pole-pieces, 10 cm. long, 3 cm. wide, 1 cm. high, of two similar electromagnets. Hence the first one-third and the last one-third parts of the wire were in a periodic field of force, while the middle one-third part containing the sphere was unrestricted in space. The apparatus was placed inside a tank with glass sides, 3 ft. long,  $1\frac{1}{2}$  ft. broad, and 2 ft. high. A small direct current about one-third of an ampere in the wire and an alternating current of about two amperes through the magnets maintained a steady vibration of the wire in air in the vertical plane if its tension was adjusted for resonance. Kerosene oil (viscosity  $\mu = 1.67 \times 0.0088$ ) was poured into the tank, the currents were increased to about half an ampere and four amperes respectively, and the tension to produce resonant vibration was determined. Amplitude of the vibration was observed with a telemicroscope having a glass scale

\* 'Collected Papers,' vol. iii. p. 52.

in the eyepiece. Correct tension could be determined within one per cent. in air and two per cent. in oil. A preliminary experiment with the wire alone without the sphere showed general agreement with Stokes's tabulated value for thin cylinders.

Three determinations were made: first with a pith ball coated with lead foil and then with gelatine-glycerine cement to make it impervious to kerosene oil, second with another pith ball covered with aluminium paint and then with the gelatine-glycerine cement, and third with a polished hollow silver ball. Gelatine melted with a little glycerine produced a cement insoluble in kerosene and was therefore used for fixing the balls on the wire.

	1st Ball.	2nd Ball.	3rd Ball.
Mass of ball in air .....	2.1307	1.1847	1.5035 gram.
Mass of oil displaced by ball .....	1.8614	1.1172	2.1323 gram.
Diameter of ball .....	1.7	1.36	1.7 cm.
Diameter of wire .....	0.0182	0.0182	0.0235 cm.
Wt. in air of 30 cm. of wire.....	0.0584	0.0584	0.1011 gram. wt.
Wt. of oil displaced by wire .....	0.0059	0.0059	0.01 gram. wt.
Best value for tension in air.....	1530	780	1010 gram. wt.
Best value for tension in oil .....	2310	1210	1840 gram. wt.
The value of $k$ obtained by Exp....	.584	.585	.580
The value of $k$ by Stokes's Theory.	.530	.536	.530

The excess of the experimental results over the theoretical ones, though small, is larger than the possible errors of experiment. In all the three cases the quantity

$$\{1 + \sigma l / 6(m_1 + km_2) \div 1 + \sigma l / 6m_1\}^2$$

was equal to 1 correct to two places of decimals, and therefore the approximations used therein could not sensibly affect the calculation. The alternating current was taken from the town supply, and in answer to a query the Chief Electrical Engineer of the Electric Supply Company wrote: "The frequency is kept constant at all times at 50 periods. There is a remote possibility of a very slight variation for a few seconds while turbines are being changed over. This would not amount to more than 1 per cent. at the outside. As the turbines are changed over not more than two or three times in the 24 hours, any slight variation would be only momentary." As has been pointed out before, the actual value of the frequency does not matter if it is constant during a determination. The wire when inside the liquid was not sensibly heated. As is required by the hydrodynamical theory, the centre of the sphere performed *small*

*periodic vibrations in a straight line* without any rotation, but possibly the velocities were not so small that their squares could be neglected. Gilbert Cook \* has found experimentally that the frictional resistance to the gravitational fall of a sphere inside water, being mainly due to skin friction and eddy formation, is proportional to the square of the velocity. The spheres were about 7 cm. below the liquid surface and about 15 cm. above the bottom of the tank. The magnets and armatures were 5 cm. on either side. The maintained oscillation in air was relatively of much larger amplitude than in the liquid. The effect of large amplitude in air, the restriction of space due to the magnets in the neighbourhood, and the increased frictional resistance due to the square law will all tend to approximate the experimental and the theoretical values.

University College, Rangoon.

May 20, 1923.

*Postscriptum dated Oct. 4, 1923.*—Prof. Barnes's paper cited above, a copy of which was obtained only a few days ago, contains a footnote that Chevalier Du Buat in Volume 2 of the second edition of his '*Principes d'Hydraulique*,' Paris, 1786, had already announced what was practically Stokes's law, and that Du Buat's experiments gave .585 for the coefficient of the inertia increase due to the fluid carried by the sphere.

CXII. *Electronic Conduction in Metals.* By ARTHUR BRAMLEY, *Fellow in Physics, Princeton University* †.

THE theory of metallic conduction owes its foundation primarily to the researches of Drude and Sir J. J. Thomson. The former introduced the conception of the free electron into the theory: this theory, however, encountered unsurmountable difficulties in the phenomena observed by Kamerlingh Onnes at low temperatures, and has gradually been superseded by the doublet theory due to J. J. Thomson, according to which the electric current is due to the influence of the external field on the orientation of the doublets. The object of this discussion is the derivation of (and expression for) the law of force, operative near the nucleus, and the explanation of the doublet structure assumed in that theory.

\* Phil. Mag. vol. xxxix. (1920).

† Communicated by Prof. E. P. Adams.

*Atomic Structure.*

We shall first calculate the magnetic and electric forces at any point in space due to the revolution of a single electron in a circular orbit about a positive nucleus with constant angular velocity.

In order to carry out the calculation, it is necessary, following the method initiated by Kirchhoff, to consider the types of solution of the differential equation for the potential.

The potentials are defined in the equations :

$$\nabla^2 \phi - \frac{1}{c^2} \frac{\partial^2 \phi}{\partial t^2} = -\rho,$$

and

$$\nabla^2 U - \frac{1}{c^2} \frac{\partial^2 U}{\partial t^2} = -\rho V/c.$$

The intensities are obtained by differentiation :

$$E = -\frac{1}{c} \frac{\partial U}{\partial t} - \text{grad } \phi,$$

$$H = \text{rot } U.$$

As a result of this calculation, we find

$$E_R = \frac{e}{4\pi} \frac{1}{\sqrt{1-\beta^2}} \cdot \frac{r - R \cos \theta_1}{(r^2 + R^2 + z^2 - 2rR \cos \theta_1)^{3/2}},$$

$$E_z = \frac{e}{4\pi} \frac{1}{\sqrt{1-\beta^2}} \cdot \frac{z}{(r^2 + R^2 + z^2 - 2rR \cos \theta_1)^{3/2}},$$

$$E_\theta = \frac{e}{4\pi} \frac{1+\beta^2}{1-\beta^2} \cdot \frac{R \sin \theta_1}{(r^2 + R^2 + z^2 - 2rR \cos \theta_1)^{3/2}},$$

$$H_\theta = 0,$$

$$H_z = \frac{e}{4\pi} \frac{\beta}{\sqrt{1-\beta^2}} \cdot \frac{r - R \cos \theta_1}{(r^2 + R^2 + z^2 - 2rR \cos \theta_1)^{3/2}},$$

$$H_R = \frac{e}{4\pi} \frac{\beta}{\sqrt{1-\beta^2}} \cdot \frac{-z}{(r^2 + R^2 + z^2 - 2rR \cos \theta_1)^{3/2}},$$

where  $(r^2 + R^2 + z^2 - 2rR \cos \theta_1)^{1/2}$

= distance from centre of electron to point in question for intensity,

R = radius of electronic orbit,

$\theta_1$  = angle between radius vector to electron and projection of  $(r^2 + R^2 + z^2 - 2rR \cos \theta_1)^{1/2}$  on orbital plane,

$\beta$  = velocity / c.

The field obtained in this case corresponds to the field produced by the simplest Bohr atom—hydrogen—when the single electron is in a non-radiating state: *i. e.*, is revolving about the nucleus in one of the quantum rings.

On account of the non-symmetrical distribution of charge, the electric and magnetic intensities at any point vary with the time, being periodic functions with period equal to that of the revolving electron\*.

### *Geometrical Considerations.*

The most fundamental property of space is that its points form a three-dimensional manifold. That is, the relationship of any given point with respect to the other point can be expressed by means of three quantities—the coordinates of the new point with respect to the old. Another familiar example of a three-dimensional manifold is the Gibbs's thermodynamic diagram, in which the properties of substances are represented in a three-dimensional manifold whose coordinates of reference are volume, entropy, and energy. The adiabatic expansion of a gas is represented by paths, straight lines in this case, parallel to the volume axis. The possible positions of a rigid body can be represented by points in a six-dimensional manifold, while the possible configurations of a system of  $n$  degrees of freedom constitute, in general, an  $n$ -dimensional manifold. The characteristic of an  $n$ -dimensional manifold is that each of the elements composing it may be defined by giving  $n$  quantities—the coordinates.

If we take any two points in a three-dimensional manifold,  $P(x, y, z)$  and  $Q(x_1, y_1, z_1)$ , then the distance between these two points is, by the fundamental proposition of Euclidean geometry (Pythagorean Theorem),

$$s^2 = (x - x_1)^2 + (y - y_1)^2 + (z - z_1)^2 ;$$

or, if we take these points infinitely near to one another, so that

$$P = P(x, y, z)$$

$$\text{and} \quad Q = Q(x + dx, y + dy, z + dz)$$

then this distance becomes.

$$ds^2 = dx^2 + dy^2 + dz^2.$$

\* Bramley, Phil. Mag. October 1922, p. 720.

Similarly, for an  $n$ -dimensional Euclidean geometry, the differential distance between  $P(x_1 \dots x_n)$  and  $Q(x_1 + dx_1 \dots)$  is

$$ds^2 = dx_1^2 + dx_2^2 \dots dx_n^2.$$

The natural extension of this idea, which was first pointed out by Riemann, is to consider the case where the fundamental form, as it is called, may be expressed in the form

$$ds^2 = g_{11}dx_1^2 + 2g_{12}dx_1dx_2 \dots g_{nn}dx_n^2,$$

where  $ds^2$  measures the infinitesimal distance between two neighbouring points in a more general manifold than that conceived by Euclid.

The distance between two given points,  $P(x_1 \dots x_n)$  and  $Q(x_1 \dots x_n)$ , measured along a definite curve, will be

$$s = \int ds = \int \sqrt{\sum g_{ij} \frac{dx^i}{dt} \frac{dx^j}{dt}} \cdot dt,$$

where the path of integration is along the simple curve connecting these two points.

This idea of gaining knowledge of the external world through a consideration of its infinitesimal parts is one which transcends physics as well as mathematics. From a knowledge of the way in which the velocity of a particle changes on the infinitesimal length of a path, we can find the time taken to traverse a certain distance along that path: so, in Riemannian geometry, from a knowledge of the distance between every two infinitely near points, we can calculate the distance between points a finite distance apart. This principle is the basis of Differential Geometry.

A difficulty may have been noticed in this presentation with respect to the measure of distance. Suppose, for example, that we have to find the distance between two points on the  $x_1$  axis,  $x_1=0$  and  $x_1=10$ , say, in a manifold in which

$$g_{11} = x_1^2.$$

Then

$$s = \int_0^{10} \sqrt{x_1^2 \left( \frac{dx_1}{dt} \right)^2} \cdot dt = \int_0^{10} x_1 dx_1 = 50.$$

The distance between them is 50, whereas we have only measured the length along the  $x_1$  axis from  $x_1=0$  to  $x_1=10$ .

The solution is obvious. The system of coordinates allows us only to label each point—i. e., when we are given the set of numbers  $x_1=10, x_2=x_3 \dots =0$ , we are able to pick out a definite point in space which is characterized by this label. But to return to the measure of distance: if we wish to find

the distance between  $x_1=0$  and  $x_1=10$  along the  $x_1$  axis, we take a measuring rod (our unit) and, starting from  $x_1=0$ , measure on this unit the length between  $x_1=0$  and  $x_1=dx_1$ , and so on, until we come to  $x_1=10$ ; then the sum of all these measurements gives us the length between  $x_1=0$  and  $x_1=10$  measured along the  $x_1$  axis with one definite unit rod. In a Euclidean manifold, we first choose the coordinate axis and then choose the points on them corresponding to  $x_1=1, x_1=2, \dots$ , etc., so that the distance between  $x_1=1$  and  $x_1=0$  etc. is unity when measured on the definite rod we are given.

If we change our rod, then this simple relation will no longer hold, provided the new rod is not identical with the old. A manifold is thus completely defined, in the Riemannian sense, when we have labelled every point with reference to a given coordinate system, and, further, have been given a unit of measurement. Riemann defined his unit of measurement by means of the equation

$$ds^2 = \sum_{ij} g_{ij} di dx^j.$$

Now this system is not yet completely defined: the ambiguity still existing was first pointed out by Weyl. Suppose we wish to compare the distance between a set of points at A and another set at B. In order to do this, we must first measure the distance between the points at A on our measuring rod, next carry it from A to B, and then measure the distance between the points at B. But how do we know that we will get the same value for this comparison if we move the measuring rod from A to B by different paths? We don't. Thus, in order to measure this ratio, we must not only fix our standard of measurement, but also the path along which this measure is transported between the given points. In general, in order completely to define our manifold, we must determine first a coordinate system through which we can identify the points in the manifold, and next place at each point in this manifold a measuring rod which is associated with this point only. Then, if we choose any path between two points A and B, the length along any curve connecting these points will be the sum of the measurements at all points P of this path, of the distance between  $P(x_1 \dots x_n)$  and  $P(x_1 + dx_1 \dots dx_n)$  measured on the rod at the point P.

If the manifold is calibrated in a definite manner by giving at each a definite measuring rod, and if we take the



measuring standard at any point  $P(x_1 \dots x_n)$  and move it to a neighbouring point  $\bar{P}(x_1 + dx \dots)$ , then there will be a relation between the length of the standard associated with the point  $P$  as measured by the standard at  $P$  and its original length as measured by itself; or, if  $dl$  is the change in length,

$$\frac{dl}{l} = -d\phi(x_1 \dots x_n).$$

If we now associate with each point a new set of standards, such that  $\bar{l}$ , the length of the new standard measured in terms of the old standard, satisfies the equation

$$\bar{l} = \lambda l, \quad \lambda = \lambda(x_1 \dots x_n),$$

then, as before,

$$\frac{d\bar{l}}{\bar{l}} = -d\phi$$

or

$$d\bar{\phi} = d\phi - d \log \lambda.$$

In order that we can find a  $\lambda$  such that  $d\phi=0$ ,

$$d\phi = d \log \lambda \text{ (a differential form)}$$

or

$$d\phi = \sum_i \psi_i dx^i, \quad \psi_i = \psi_i(x_1 \dots x_n).$$

Thus the metrical character of a manifold is characterized relatively to a system of reference by two fundamental forms, namely a quadratic differential form,

$$ds^2 = \sum g_{ij} dx^i dx^j,$$

and a linear one,  $d\phi = \sum \psi_i dx^i$ .

If the calibration is changed,  $\psi_i$  and  $g_{ij}$  must be replaced by

$$\psi_i - \frac{1}{\lambda} \frac{\partial \lambda}{\partial x^i} \quad \text{and} \quad \lambda g_{ij}.$$

In four-space ( $x, y, z, t$ ),

$$\frac{dl}{l} = \psi_1 dx_1 + \psi_2 dx_2 + \psi_3 dx_3 + \psi_4 dx_4.$$

Integrating,

$$\log l/l_0 = \int (\psi_1 dx_1 + \psi_2 dx_2 + \psi_3 dx_3 + \psi_4 dx_4),$$

and the length  $l$  will be independent of the path, provided

$\psi_1 dx_1 + \psi_2 dx_2 + \psi_3 dx_3 + \psi_4 dx_4$  is a perfect differential. The condition for this is

$$\begin{aligned} \frac{\partial \psi_3}{\partial y} - \frac{\partial \psi_2}{\partial z} &= 0, & \frac{\partial \psi_1}{\partial z} - \frac{\partial \psi_3}{\partial x} &= 0, & \frac{\partial \psi_2}{\partial x} - \frac{\partial \psi_1}{\partial y} &= 0, \\ -\frac{\partial \psi_4}{\partial x} - \frac{\partial \psi_1}{\partial t} &= 0, & -\frac{\partial \psi_4}{\partial y} - \frac{\partial \psi_2}{\partial t} &= 0, & -\frac{\partial \psi_4}{\partial z} - \frac{\partial \psi_3}{\partial t} &= 0. \end{aligned}$$

If  $\psi_1, \psi_2, \psi_3$ , and  $\psi_4$  were the potentials of the electromagnetic field, these equations would give us precisely the three components of the electric and magnetic forces which are zero in this case.

Natural phenomena must obviously be independent of the particular coordinate system we use, or the particular standards of length at each point in the manifold. Accordingly, all quantities or relations that represent these conditions analytically must contain the functions  $g_{ij}$  and  $\psi_i$  in such a way that invariance holds:

(i.) For any transformation of coordinates (coordinate invariance) :

(ii.) For the substitutions which replace  $g_{ij}$  and  $\psi_i$  by  $\lambda g_{ij}$  and  $\psi_i - \frac{\partial}{\partial x_i} \log \lambda$  respectively, no matter what function of the coordinate  $\lambda$  may be (calibration invariance).

When we are given the  $g$ 's and  $\psi$ 's, the calibration and coordinate invariance enables us to determine all the physical properties which are represented by this manifold.

In order to determine the  $g$ 's, we shall assume that our manifold is of such a character that the trajectories of the particles in which we are interested for our special problem (mechanical) will be geodesics in the manifold. This assumption, which is tacitly assumed by Einstein and other workers in this field, really amounts to a device for integrating the differential equations of motion of the particle. The geodesic path along which a particle moves under the action of no forces will be given by the equation

$$g_{ik} \frac{d^2 x^i}{ds^2} + \Gamma_{rk} \frac{dx^r}{ds} \frac{dx^s}{ds} = 0,$$

where

$$ds^2 = \sum_{ik} g_{ik} dx^i dx^k$$

and

$$\Gamma_{rk} = \frac{1}{2} \left( \frac{\partial g_{rk}}{\partial x^s} + \frac{\partial g_{sk}}{\partial x^r} + \frac{\partial g_{rs}}{\partial x^k} \right).$$

If we define

$$H = \sum_{ik} \rho_0 g_{ik} \frac{dx^i}{ds} \frac{dx^k}{ds} = \rho_0,$$

then our equation may be written

$$\frac{d}{ds} \left( \frac{\partial H}{\partial \dot{x}^r} \right) - \frac{\partial H}{\partial x^r} = 0.$$

If we are given a problem of a particle under the action of no forces, whose kinetic energy

$$T = \sum_i \rho_0 \left( \frac{dx^i}{ds} \right)^2,$$

then from a comparison with the above equation we see that

$$g_{ij} = 0 \quad \left. \begin{array}{l} i \neq j \\ i = j, \end{array} \right\} \rho_0,$$

or the manifold is Euclidean.

When the particle is under the action of no forces, the problem has as yet not in general been solved, although Schwarzschild has found a solution for the case of a particle under the action of the gravitational field of a spherical body.

For this case, in polar coordinates,

$$ds^2 = - \left( 1 - \frac{2m}{r} \right)^{-1} dr^2 - r^2 d\theta^2 - r^2 \sin^2 \theta d\phi^2 + \left( 1 - \frac{2m}{r} \right) dt^2,$$

where  $m$  = mass of attracting body.

We shall show, in the sequel, how the potential  $\psi$  of the electric field corresponding to a positive nucleus can be found from a knowledge of the  $g$ 's, subject to the above restrictions.

To test our new hypothesis—the invariant character of physical laws—we must choose an initial invariant law, and work out its implication. We shall choose as our initial law a Hamiltonian principle—that the change in our fundamental integral invariant  $\int H dx$  is zero for every small variation of the structure of the manifold.

In the case of a change of coordinates, the integral must be expressed in invariant form, *i.e.* we must express the law in the following way:

$$\delta \int H \sqrt{-g} dx_1 \dots dx_4 = \delta \int H dx = 0,$$

where

$$H = H \sqrt{-g}.$$

Since every Riemannian space possesses an integral of

this form\*, the laws of perfect fluids which follow as a natural consequence of its invariance must be valid in all Riemannian spaces.

In the case of a change in the calibration of the universe, the integral must be expressed in slightly different form, namely:

$$\delta \int H dx = 0.$$

Since the density  $\rho_0$  is of weight zero (see sequel, p. 1067), the tensor density  $H$  is a calibration invariant, and thus we are led to the above form as the correct expression of the Hamiltonian law, in the case of electromagnetic phenomena.

First consider the case where we subject the manifold to a continuous deformation, so that the point  $x_i$  becomes transformed into the point

$$\bar{x}_i = x_i + \xi(x_1 \dots x_n) \cdot \epsilon,$$

where  $\epsilon$  is an infinitesimal parameter (Lie's transformation). Then

$$\delta \int H dx = \int \frac{\partial(H\xi^i)}{\partial x^i} dx + \int \delta H \cdot dx,$$

where the first integral represents the change in  $H$  due to a change in the contour of the region of integration (*i. e.*, a change in the limits of integration).

Now, since we can write

$$-\delta H = H_i^k \frac{\partial \xi^i}{\partial x^k} + \frac{1}{2} \frac{d\eta_{rs}}{dx_i} \cdot H^{rs} \xi^i \quad (\text{summed}) :$$

defining

$$V_i^k = H_i^k - \delta_i^k \cdot H,$$

where

$$\delta_i^k = \begin{cases} 0 & i \neq k \\ 1 & i = k \end{cases},$$

the equation becomes

$$-\delta \int H dx = \int \frac{\partial(V_i^k \xi^i)}{\partial x^k} dx + \int \left\{ -\frac{\partial H_i^k}{\partial x^k} - \frac{1}{2} \frac{\partial \eta_{rs}}{\partial x^i} \cdot H^{rs} \right\} \xi^i dx.$$

Therefore

$$\frac{\partial(V_i^k \xi^i)}{\partial x^k} = V_i^k \frac{\partial \xi^i}{\partial x^k} + \frac{\partial V_i^k}{\partial x^k} \xi^k = 0;$$

$$i. e., \quad V_i^k = 0, \quad \text{or} \quad \delta_i^k \cdot H = H_i^k,$$

and also

$$H_i^k = \frac{\partial H_i^k}{\partial x^k} + \frac{1}{2} H^{rs} \frac{\partial \eta_{rs}}{\partial x_i} = 0.$$

\* L. P. Eisenhart, Proc. Nat. Acad. January 1923, p. 4.

Now the equation above is equivalent to the general equation of a fluid under the action of forces.

Assuming Euclidean coordinates, *i. e.* a fluid under the action of no forces, the equation can be written

$$\frac{\partial H_i^k}{\partial x^k} = 0.$$

The velocity  $u = \frac{dx}{ds}$  etc. may be written as two parts, the first referring to the motion  $u_0$  etc. of the centre of mass of the particle in an element, the second to the interior motion  $u_1$  etc. relative to the centre of mass. With regard to the last part,  $\Sigma \rho u_1 v_1$ , for instance, represents the rate of transfer of  $u$ -momentum across unit area parallel to the  $y$ -plane, and is therefore equivalent to the stress usually denoted by  $p_{xy}$ .

Taking  $i=4$ , we get the well-known equation of continuity :

$$\frac{\partial(\rho u_0)}{\partial x} + \frac{\partial(\rho_0 v)}{\partial y} + \frac{\partial(\rho_0 w)}{\partial z} + \frac{\partial \rho}{\partial t} = 0.$$

Taking  $i=1$ ,

$$-\left(\frac{\partial p_{xx}}{\partial x} + \frac{\partial p_{yy}}{\partial y} + \frac{\partial p_{zz}}{\partial z}\right) = \rho \frac{\partial u_0}{\partial t},$$

where we have taken

$$g_{ik} = \begin{cases} 0 & i \neq k \\ 1 & i = k. \end{cases}$$

Accordingly, the whole of the dynamics of material systems is contained in the integral invariant equation; further, from the consideration of calibration invariant conditions associated with the Hamiltonian integral, we shall find that the electromagnetic laws of the field are a consequence of the invariant nature of the equations. The prediction of these well-known properties of matter seems to be a valuable confirmation of the theory, aside from its intrinsic value as an explanation of gravitational forces, and further, as we shall see, of the interatomic dynamics.

We have here to add the further restriction that the Hamilton Principle must also be invariant with respect to re-calibration, in which  $\psi_i$  and  $g_{ik}$  are replaced respectively by  $\psi_i - \frac{\partial}{\partial x_i} \log \lambda$  and  $\lambda g_{ik}$ , where  $\lambda$  is an arbitrary function of position (positive), or if the calibration ratio between the altered and the original calibration is  $\lambda = 1 + \pi$ ,

where  $\pi$  is an infinitesimal scalar. As a result of this process, the fundamental quantities assume the following increments :

$$\delta g_{ik} = \pi g_{ik} \quad \text{and} \quad \delta \psi_i = -\frac{\partial \pi}{\partial x_i}.$$

Since the variation of the action must vanish,

$$\delta \int H dx = \int \frac{\partial}{\partial x^k} (\delta v^k) dx + \int (W^i \delta \psi_i + \frac{1}{2} W^{ik} \delta g_{ik}) dx = 0,$$

where  $W^i = \frac{\partial H}{\partial \psi_i}$  and  $\delta v^k$  is defined uniquely by the above equation.

Substituting in the equation the above values of  $\delta g_{ik}$  and  $\delta \psi_i$ , and further setting

$$\delta v^k = \pi \cdot s^k + \frac{\partial \pi}{\partial x^r} \cdot h^{kr}.$$

Then

$$\begin{aligned} \delta \int H dx = & \int \frac{\partial^2 \pi}{\partial x^r \partial x^s} h^{rs} + \int \frac{\partial \pi}{\partial x^k} \left( s^k + \frac{\partial h^{rk}}{\partial x^r} - W^k \right) dx \\ & + \int \pi \left( \frac{ds^k}{dx^k} + \frac{1}{2} W_i^i \right) dx, \end{aligned}$$

from which we have at once

$$s^k + \frac{\partial h^{rk}}{\partial x^r} = W^k,$$

$$h^{kr} + h^{rk} = 0,$$

$$\frac{\partial s^k}{\partial x^k} + \frac{1}{2} W_k^k = 0.$$

Now, for charge-free space  $W_k^k = 0$ , so that we have at once

$$\frac{\partial s^k}{\partial x^k} = 0,$$

and further, as a consequence of differentiating the first, since we have

$$\frac{\partial^2 h^{rs}}{\partial x^r \partial x^s} = 0,$$

$$\frac{\partial W^i}{\partial x^i} = 0.$$

The last equation is therefore satisfied, provided  $W^i = f_i(r)$  only, for we shall take

$$W^1 = W^2 = W^3 = 0.$$

If the variation vanishes on the boundary considered—i. e., if we can neglect the boundary integral over the surface of the charges, since the variation is necessarily zero over the infinite boundary,—we have

$$\int \delta H \, dx = \int (W^i \delta \psi_i + \frac{1}{2} W^{ik} \delta g_{ik}) \, dx = 0;$$

so that

$$W^i = 0 \quad \text{and} \quad W^{ik} = 0,$$

and we get at once, exactly Maxwell's equation for free space :

$$s^i + \frac{\partial h^{ri}}{\partial x^r} = 0, \quad s^i = 0.$$

We have thus exactly verified Maxwell's equation for the conditions under which they are valid, since in that case we can neglect the surface integral of the flux over free space and near objects of low electrification.

#### *Potentials and Intensities.*

A fundamental calibration invariant is expressed by the following differential equation :

$$\left\{ \psi_i + \frac{\partial}{\partial x^i} \log g_{jk} \right\} = f_i \left( \frac{g}{g} \right),$$

where  $f_i \left( \frac{g}{g} \right)$  is an arbitrary function.

The solution for the last differential equation for the  $\psi$ 's allows us to solve for them when the  $g$ 's are given, thus determining the character of our manifold completely. The fact that the  $g$ 's allow us to determine the  $\psi$ 's is at once evident from the fact that we have chosen the  $g$ 's so that the paths of the particles are geodesics. Knowing the path of an electron around a positive nucleus would enable us to determine the law governing the forces acting on the electron ; in fact, for the astronomical case it is precisely the above process of reasoning that led Newton to postulate the laws of gravitational attraction between material bodies.

Thus

$$\frac{\partial g_{jk}}{\partial x^i} + g_{jk} \cdot \psi_i = f_i \cdot g_{jk} = f_{ijk},$$

which is our fundamental differential invariant.

For the differential fundamental form,

$$ds^2 = H_1^2 dx_1^2 + H_2^2 dx_2^2 \dots H_4^2 dx_4^2,$$

our equation becomes

$$\frac{\partial H_i^2}{\partial x^i} + H_i^2 \cdot \psi_i = \bar{f}_i \quad (\text{not summed}).$$

Applying integrability conditions, we obtain

$$\frac{\partial H_i^2 \psi_i}{\partial x^k} - \frac{\partial H_k^2 \psi_k}{\partial x^i} = \frac{\partial \bar{f}_i}{\partial x^k} - \frac{\partial \bar{f}_k}{\partial x^i} = F_{ik}.$$

From these equations results

$$\frac{\partial F_{ik}}{\partial x^j} + \frac{\partial F_{kj}}{\partial x^i} + \frac{\partial F_{ji}}{\partial x^k} = 0,$$

which is Maxwell's first set of equations, where the  $F_{ik}$  are the components of the intensity of the field; so that a knowledge of the function  $\bar{f}_i$  would enable us to determine the electric and magnetic intensities of the field. We have, moreover, been able to derive all of Maxwell's equations from the consideration of invariant forms, which, with the previous discussion of the equations of dynamics, completes the determination of the phenomena of nature represented by our manifold.

From a consideration of the equations of dynamics, we can derive the form of the kinetic energy (so-called energy tensor) for an electron under the influence of a positive nucleus. Thus we find

$$-ds^2 = \left(1 - \frac{2e}{r}\right)^{-1} dr^2 + r^2 d\theta^2 + r^2 \sin^2 \theta d\phi^2 - \left(1 - \frac{2e}{r}\right) dt^2,$$

where  $e$  is a constant depending on the character of the nucleus; the only condition imposed on the nucleus is that it is very small in comparison with the path of the electron.

Thus

$$g_{11} = -\left(1 - \frac{2e}{r}\right)^{-1}, \quad g_{22} = -r^2, \\ g_{33} = -r^2 \sin^2 \theta, \quad g_{44} = \left(1 - \frac{2e}{r}\right).$$

We shall now proceed to calculate the  $\psi$ 's, and thus derive the laws of force acting on the particle, through Maxwell's equation.



Taking our differential invariant in the form

$$g_{44} \cdot \psi_4 = f_4(r) = -V,$$

where  $V$  = potential of the nucleus, since the  $g$ 's do not explicitly contain the time, and the propagated potentials  $\psi_1 = \psi_2 = \psi_3 = 0$  for our particular case.

There is another important consideration as to why the potential should be of the above form. This choice for the potential is of weight one, while the  $\psi$ 's themselves, assumed by Weyl as the components of the potential function, are of weight zero. The weight of an element is defined as the power of  $\lambda$  which the element is multiplied by if the calibration is changed—*e. g.*,

$$g_{ij} \rightarrow \lambda g_{ij} \quad \text{of weight one,}$$

$$g_{ik} \frac{dx^i}{ds} \frac{dx^k}{ds} \rightarrow g_{ik} \frac{dx^i}{ds} \frac{dx^k}{ds} \quad \text{of weight zero.}$$

We shall now, since the choice of the potential is intimately connected with this argument, briefly review the reason\* for taking the equations

$$G_{ij} - \frac{1}{2}g_{ij}G = -8\pi \cdot T_{ij}$$

as the law of gravitation; or, since the argument for the choice of the potential is independent of the particular form of the equation, any set of equations of the form

$$G_{ij} - \frac{1}{2}g_{ij}(G - \lambda) = -8\pi \cdot T_{ij},$$

where  $G_{ij}$  is the contracted curvature tensor and

$$G = G_{ij}g^{ij}.$$

The transition from discrete particles to the continuous medium involves, in Newtonian theory, the displacement of

$$\nabla^2\phi = 0 \quad \text{by} \quad \nabla^2\phi = -4\pi\rho_0.$$

We shall now find the corresponding modification of Einstein's equation

$$G_{ij} = 0.$$

Writing the Schwarzschild line element in the form

$$ds^2 = -\left(1 + \frac{2m}{r}\right)(dx^2 + dy^2 + dz^2) + \left(1 - \frac{2m}{r}\right)dt^2,$$

where the origin is now arbitrary and  $r$  denotes the distance from the attracting particle to the element  $ds$ . The effect

\* Eddington's Report, p. 59.

of a number of particles being additive, to a first approximation, we have

$$ds^2 = -(1 + 2\Omega)(dx^2 + dy^2 + dz^2) + (1 - 2\Omega)dt^2,$$

where  $\Omega$  = Newtonian potential.

Consider a point 0 in the medium where the density is  $\rho_0$ , and with 0 as centre describe an infinitely small sphere. If we neglect the matter in the sphere, the equation  $G_{ij} = 0$  will be satisfied at 0. Hence, in calculating the value of  $G_{ij}$  at 0, we need only consider the values of  $G_{ij}$  due to the matter inside an infinitely small sphere of uniform density.

Since  $\frac{\partial \Omega}{\partial x}$ , etc., vanish at 0, we have

$$G_{ii} = -\frac{1}{2}g^{11}\frac{\partial^2 g_{11}}{\partial x_1^2} + \frac{1}{2}g^{22}\frac{\partial^2 g_{11}}{\partial x_2^2} + \frac{1}{2}g^{33}\frac{\partial^2 g_{11}}{\partial x_3^2} + \frac{\partial^2}{\partial x_1^2} \log \sqrt{-g};$$

and since

$$\frac{\partial^2 g_{11}}{\partial x_1^2} = \frac{\partial^2 g_{14}}{\partial x_1^2} = -\frac{\partial^2}{\partial x_1^2} \log \sqrt{-g} = -\frac{\partial^2 \Omega}{\partial x^2}$$

we have

$$G_{ii} = \frac{\partial^2 \Omega}{\partial x_1^2} + \frac{\partial^2 \Omega}{\partial x_2^2} + \frac{\partial^2 \Omega}{\partial x_3^2} = -4\pi\rho_0,$$

and similarly

$$G_{ii} = -\pi\rho_0, \quad i = 1, 2, 3, 4.$$

Moreover, since  $G_{ii}$  is of weight zero,  $\rho_0$  is of weight zero.

Now  $G = g^{ij}G_{ij} = (-G_{11} - G_{22} - G_{33} + G_{44})I$

if we take the Galilean value of  $g^{ij}$  at the point 0, and where  $I$  is a unit scalar of weight  $-1$ , since  $g^{ij}$  is the weight of  $-1$ .

Thus  $G = 8\pi\rho_0 I = 8\pi I \cdot T$

and  $-8\pi IT_{ij} = (T_{ij} - \frac{1}{2}g_{ij}G).$

This equation shows that  $T$  is of weight zero,  $T_{ij}$  of weight one,  $T^i_k$  of weight zero.

Now consider the system of equations proposed by Einstein:

$$-8\pi IT_{ij} = G_{ij} - \frac{1}{4}g_{ij}G,$$

$$-8\pi IS_{ij} = G_{ij} - \frac{1}{4}g_{ij}G,$$

and  $T^{ij} = S^{ij} + \frac{1}{4I}(G - G_0)g_{ij},$

where  $S^k_i = F^k_{ir}F^{kr} - \frac{1}{4}F^{rs}F^{rs} \cdot \delta^k_i.$

In order to be consistent with the weighting system shown above, the potential must be of weight *one*, for  $S_{ij}$  is necessarily of weight one, since  $T_{ij}$  and  $S_{ij}$  must have the same weight in any system. The importance of this aspect of the subject of weights was emphasized by Pauli (*Enzykl.* 1921), and an attempt was made by F. Jüttner (*Math. Annalen*, 1922) to modify the Einstein equation,

$$-8\pi S_{ij} = G_{ij} - \frac{1}{4}g_{ij}G,$$

so that the various terms became of the same weight.

L. P. Eisenhart has shown (Proceedings of National Academy, April 1922) that the  $\psi$ 's in the second fundamental form are not the potentials of the field, but that the true potentials must be of weight *one*, whereas the  $\psi$ 's are of weight zero. The choice of the potential  $V$  we have defined above satisfies this restriction, and is in agreement, therefore, with the geometry of paths. (Eisenhart and Veblen \*.)

Differentiating with respect to  $g_{44}$ , we have

$$g_{44} \frac{\partial \psi_4}{\partial g_{44}} + \psi_4 = - \frac{\partial V}{\partial g_{44}}$$

or

$$- \frac{\partial \psi_4}{\partial g_{44}} = \frac{\psi_4 + \frac{\partial V}{\partial g_{44}}}{g_{44}};$$

so that

$$W^4 = \frac{-g_{44}^2}{g_{44} \frac{\partial V}{\partial g_{44}} - V},$$

and the equation satisfied by the potential is

$$-g^2_{44} = \frac{1}{c^2} \left( \frac{\partial^2 V}{\partial r^2} + \frac{2}{r} \frac{\partial V}{\partial r} \right) \left( g_{44} \frac{\partial V}{\partial g_{44}} - V \right).$$

At

$$n = 2e, \quad g_{41} = 0;$$

so that a solution of the equation at this point is

$$V = \frac{\epsilon}{r}.$$

By a change of variable  $z = \frac{1}{r}$ , our equation becomes

$$\frac{1}{c^2} \left( \frac{1}{z^4} - \frac{2e}{z^3} + \frac{4e^2}{z^2} \right) = \frac{d^2 V}{dz^2} \left\{ \left( \frac{1}{2e - z} \right) \frac{dV}{dz} - V \right\}.$$

\* Eisenhart and Veblen, *Proc. Nat. Acad.* Feb. 1922, p. 19.

Assuming a solution of the form

$$V = \sum a_n z^{m+n},$$

the equation may be written

$$\begin{aligned} & \frac{1}{c^2} \left( \frac{1}{z^4} - \frac{2e}{z^3} + \frac{4e^2}{z^2} \right) \\ &= -(m+n)(m+n-1)(m+l-1)a_n a_e z^{2m+n+l-2} \\ &+ (m+l)(m+n)(m+n-1) \frac{a_n a_e}{2e} z^{2m+n+l-3}. \end{aligned}$$

i. Now, calculating the coefficient of  $z^{2m+n+l-2}$ , we have as the coefficient for  $m=0$ ,

$$\begin{aligned} & -n(l-1)(n-1)a_n a_e + \frac{l_n}{2e} (n+1)a_{n+1} a_e \\ &+ \frac{n(l+1)(n-1)}{2e} a_n a_{e+1}. \end{aligned}$$

A solution appropriate to this expansion is

$$-V = \frac{1}{c^2} \left( \frac{r}{2} - \frac{e^2}{r} + \frac{8e^3}{r^2} + \dots \right);$$

this expansion converges for large values of  $r$ .

Now we know that

$$\frac{4e^2}{c^2} = \epsilon,$$

$\epsilon$  = charge on the nucleus which determines the constant  $e$ .

The potential is equal to

$$V = \frac{\epsilon}{r} \text{ app., } r > 10^{-5} \text{ cm.}$$

When, however, the radius becomes of the order  $10^5$ , the first term begins to predominate. The significance of this term will be discussed further when we have developed the meaning of the equation.

Collecting coefficients in a different manner, we have

$$\begin{aligned} \text{ii. } & -n(n-1)(l-2)a_n a_{e-1} - (n-1)(n-2)(l-1)a_{n-1} a_e \\ &+ nl(n-1) \frac{a_n a_e}{2e} \end{aligned}$$

as the coefficient of  $z^{n+l-3}$ .

This gives as a solution for the potential

$$V = \frac{4e^2}{\epsilon c^2} \frac{1}{r^2} + \epsilon r - \frac{\epsilon c^2}{10e} r^2 \dots,$$

where  $\epsilon$  = charge on the nucleus.

This expansion, which converges only for very small values of  $r$ , gives the value of the potential inside the singular shell, which corresponds to the value of  $r$  at which the potential becomes infinite. We note that the intensity, which is negative near the interior side of this singularity, positive on the exterior side, approaches  $\pm \infty$  at the boundary of this region.

There is a particular case, in which our equations for  $W^4$  break down, which we shall now consider.

Suppose we have

$$\tilde{f}_1 = \beta g_{14}, \quad \beta = \text{const.},$$

then we have

$$\psi_1 = \beta,$$

and further

$$W^4 = \infty.$$

Now in this case we can calculate the forces at once from our invariant differential form, we have

$$\tilde{f}_4 = \beta g_{41} = -V,$$

and the components of force are

$$F_{4r} = \frac{2Be}{r^2},$$

the other being equal to zero.

The fact that  $W^4 = \infty$  does not enter into this discussion since the derivative  $\frac{\partial H}{\partial \psi_2}$  does not exist in this case.

In this particular solution, for which Coulomb's law is verified, the calibration, in our sense, is uniform at every point.

F. Jüttner in a recent article discusses this very case, and arrives at the same solution for a spherical body

$$-V = \beta g_{44}.$$

We may notice that the potential is zero at the boundary of the nuclear universe.

The writer (Proc. Nat. Acad. 1923) has shown that if the laws of mechanics hold and the space is Riemannian, *i. e.* the functions can be expressed in the form  $\psi_i = \frac{\partial \rho}{\partial x^i}$ , where  $\rho$  is a scalar function, then the law of conservation of energy holds provided

$$S_{ij} = T_{ij} + \Delta_{ij},$$

where  $\Delta_{ij}$  has indeterminate principal directions and  $\Delta_{ii}^k = 0$ .

Now the solution

$$V = \beta g_{41} \text{ or } \psi_4 = \beta, \quad \psi_1 = \psi_2 = \psi_3 = 0,$$

satisfies this relationship, while the other solution which leads to the existence of the doublet structure cannot possibly satisfy this equation.

Thus, the inverse square law only holds in systems from which there is no radiation of energy—i. e., Maxwell's equations are only valid for quasi-stationary motion which emits no radiation. When radiation takes place, these equations have to be modified.

These conclusions are in agreement with Bohr's dynamical laws which govern the motion of electrons. In open orbits, such as those described by an  $\alpha$ -particle approaching the nucleus of an atomic system, the experiments of Rutherford show that the inverse square cannot hold.

From a consideration of the form of the differential equation, we see that the position of the pole is given by the equation

$$V = \frac{\partial \log g_{41}}{\partial r} \frac{\partial V}{\partial r}.$$

In order to prove the existence of this pole, take an infinitesimal region surrounding  $r=0$ , such that within that neighbourhood the following equality is satisfied :

$$(i.) \quad V > -n \frac{\partial V}{\partial r}, \text{ and hence } V < \frac{a}{r} :$$

$$\therefore \quad \frac{2}{r} \frac{dV}{dr} + \frac{d^2 V}{dr^2} > 0,$$

or

$$r \frac{d^2 V}{dr^2} + V > 0 \text{ within the neighbourhood of } r=0,$$

or

$$\frac{4e^2}{a} > 0, \quad a = \text{finite quantity},$$

which is impossible.

$$(ii.) \quad V = -r \frac{dV}{dr},$$

$$g_{41}^2 = 0,$$

which is also impossible; so that we must have

$$(iii.) \quad V < -r \frac{dV}{dr} :$$

$$(a) \quad \frac{dV}{dr} = -\sigma^2,$$

then the denominator of the right-hand side is positive, and hence a pole exists in the region  $2e > r > 0$ ;

$$(b) \quad \frac{dV}{dr^2} = +\sigma^2,$$

since at  $r=2e$ ,

$$\frac{dV}{dr} = -\frac{\epsilon}{r^2},$$

$$\frac{dV}{dr} = \frac{d^2V}{dr^2} = 0 \text{ at some point in this region,}$$

which is impossible.

Therefore  $V$  becomes infinite within the region

$$2e > r > 0.$$

The experimental investigations of Rutherford on the bombardment of nuclei by  $\alpha$ -particles show that the electric intensity becomes infinite in the region of the nucleus,  $r < 10^{-12}$ , which is in agreement with the character of the differential equation. The change in the sign of the intensity in the immediate vicinity of the singular shell accounts, moreover, for the fact that all the negative charges in the universe have not been neutralized.

Return, now, to a consideration of the solution in expansion within the singular shell; the potential is given by the series

$$V = \frac{4e^2}{\epsilon c^2} \cdot \frac{1}{r^2} + \epsilon r - \frac{\epsilon r^2}{10e} \cdot r^2 \dots\dots,$$

which approaches  $\frac{4e^2}{\epsilon c^2} \cdot \frac{1}{r^2}$  as  $r \rightarrow 0$ .

Outside, we obtain the solution

$$-V = \frac{1}{c^2} \left( \frac{r}{2} - \frac{4e^2}{r} + \frac{8e^2}{r^2} - \frac{8e^4}{3r^3} \dots\dots \right),$$

which gives within the range  $10^5 > r > 10^{-10}$ ,

$$V = \frac{\epsilon}{r} \text{ to a first approximation.}$$

When, however,  $r > 10^5$ ,

$$V = -\frac{r}{2c^2}.$$

This anomaly is due to the presence of world electricity

in an analogous manner to the existence of world matter postulated for the maintenance of the universe.

When  $r=2e=10^5$  app.,  $g_{44}=0$ , *i. e.* the time component stands still while  $g_{11}=\infty$ , so that we have reached the end of the nuclear universe. The finite universe of the nucleus, viewed from an exterior point, has many properties common to the stellar universe of Einstein. Viewed from within, the universe seems to be of infinite spatial dimensions, while the time component seems slower and slower as we approach that infinite region becoming zero at infinite. The region beyond  $r=2e$  is altogether shut off from us by a barrier of space and time.

If we take an electron on the boundary of this nuclear region  $r=2e$ , and let it move under the action of the nucleus, it will finally fall towards the nucleus, taking up a position on the singular shell beyond which it is unable to pass. We have, therefore, in our system a stable electric doublet composed of the nucleus and the electron, whose moment  $M$

$$M=10^{-22} \text{ electrostatic unit.}$$

This stable doublet system is assumed by Sir J. J. Thomson in his work on electronic conduction. The effect of the external field on the direction of the doublets gave, as we have seen in the introduction, qualitative results which agree with experiment at all temperatures. A similar construction has been assumed by Abraham to account for high-frequency currents and radiation from antennæ. For high-frequency currents the electron is not shot out of the atom, but oscillates about the position of equilibrium, generating the electric waves which appear in this case. This model, as worked out by G. W. Pierce, has given results for the radiation from bent antennæ which agree well with experiment.

### *Conclusion.*

From considerations based on Weyl's principle of invariance of calibrations, the writer has deduced the laws of force operative in the neighbourhood of the nuclear charge, which satisfy the results obtained by Rutherford on the deflexion of  $\alpha$ -particles by atomic nuclei; the existence of the doublet used by Sir J. J. Thomson in his theory of metallic conduction; and, further, the important consequence that the inverse square law only holds for charges which do not radiate energy, which agrees with the dynamics of Bohr's atomic model.

In conclusion, the writer wishes to express his gratitude to Professor E. P. Adams for his interest and assistance during the writing of this paper.



CXIII. *On the Use of Medians for reducing Observations relating to several Quantities.* By Professor F. Y. EDGEWORTH, F.B.A.\*.

HEREIN are submitted some further considerations on a method which the writer proposed in the 'Philosophical Magazine,' August 1887 and March 1888, for determining several quantities connected with observations by equations many times more numerous than the sought quantities. The facility and the accuracy of the method are now to be reconsidered.

I. The directions given by Professor Turner in the improved statement of the method which he contributed to the 'Philosophical Magazine,' December 1887, are very simple; yet in applying them to concrete examples he experienced difficulties. I attempt to lighten those difficulties by restating the *rationale* of the method, and by amplifying the directions for its application.

The use of the plural median is an extension of Laplace's method of *Situation* ('*Théorie Analytique des Probabilités*,' Supplement 2). The simplest example of that method occurs when there are several observations each purporting to afford an equally good value of the *quæsitum*—say,  $r_1, r_2, \dots, r_n$ , each equalled to  $hx$ . The rule is to arrange the values of  $x$  given by these equations in the order of magnitude—say, as points on a line; and to put for  $x$  a value which has as many of the given points above as below it. When the number of observations,  $n$ , is even, this condition is fulfilled by *any* point between the values of  $x$  numbered

$\frac{n}{2}$  and  $\frac{n}{2} + 1$  in the order of magnitude. Now, let the coefficient  $h$  be different for different observations, while the error to which an observation is liable—the actual or absolute, as distinguished from the percentage, error—is the same for all the observations. We shall then have  $n$  equations of the form  $h_1x - r_1 = 0, h_2x - r_2 = 0 \dots$ ; from which  $n$  values of  $x$  may be extracted. These values—say,  $x_1, x_2, \dots, x_n$ —are then to be arranged in the order of magnitude, and each multiplied by the corresponding value of  $h$ . Then for  $x$  there is to be taken a value such that the sum of the expressions of the type  $h_i(x - x_i)$ ,  $x > x_i$  should as nearly as possible be equal to the sum of the quantities  $h_i(x_s - x)$ ,  $x < x_s$ . In other words, the sum of the weighted

\* Communicated by the Author.

residuals (using weight in a somewhat special sense), each taken in absolute quantity, say

$$\Sigma h_r | x - x_r | ,$$

is to be as small as possible. This condition is analogous to that which constitutes the Method of Least Squares, viz. that the sum of the squares of the said residuals should be a minimum (see as to the analogy, Phil. Mag. 1888, vol. xxv. p. 185). The required point may or may not coincide with one of the given points  $x_1, x_2, \dots x_n$ . The coincidence is necessary when the sum of the products of type  $h_r x_r$  is odd; and it becomes very probable, even when that sum is even, if the weights  $h_1, h_2, \dots$  are of very various sizes.

When we go on to the case of two *quasita*, two dimensions in space, we have for the analogue of given points given lines of the type

$$x \cos \theta_r + y \sin \theta_r - v_r ;$$

each of these being multiplied by a coefficient corresponding to the worth of the observation, the sum of the weighted residuals, each in absolute magnitude, say

$$\Sigma h_r | x \cos \theta_r + y \sin \theta_r - v_r | ,$$

is to be as small as possible. If the data are in the form  $a_r x + b_r y = c_r$ , where  $c_r = \sqrt{a_r^2 + b_r^2} \times v_r$ , the  $v$ 's being observations of equal worth (in the sense above defined); the expression to be minimised, viz.

$$\Sigma | a_r x + b_r y - c_r | ,$$

becomes identical with the above by putting  $h_r = \sqrt{a_r^2 + b_r^2}$ .

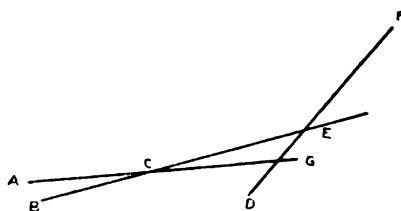
The search for the required point  $(x, y)$  may be facilitated by the following proposition. If through  $(x, y)$  is drawn a line parallel to the axis of  $x$ , and on it are marked the points  $x_1, x_2, \dots x_n$  at which it intersects lines given by the observations, then the point  $(x, y)$  is the median of the points  $x_1, x_2, \dots x_n$ ; and the like is true of a line drawn through  $(x, y)$  parallel to the axis of  $y$ . For the sum of the weighted residuals, which is to be minimised, may be written

$$\Sigma | x h_r \cos \theta_r + y h_r \sin \theta_r - h_r v_r | .$$

If now the median of the points of intersection is not  $x$ , let it be  $x'$ . Then, substituting  $x'$  for  $x$  in the above written expression, we shall obtain a smaller value for the sum. The proposition is not convertible. A point which fulfils the above condition secures what is in a certain sense a *minimum*

value, but not necessarily the *least possible* value for the sum of weighted residuals. Accordingly, the required point is not always secured by the rule at first proposed (Phil. Mag. July 1887), even as improved by Professor Turner (Dec. 1887). The intersection of the locus, consisting of points each of which is a median with respect to points on a horizontal with the corresponding locus for verticals, determines a minimum, but not always the *least possible* value for the sum of weighted residuals. Among the minima so determined the one which makes the sum of weighted residuals the *least possible* is to be selected. There is thus obtained what Professor Turner desiderated, an "additional criterion for extracting a single solution from the median loci" (*loc. cit.* p. 470). The trouble of selection is not likely to be considerable, since the compared points will probably be in the same neighbourhood, and accordingly the great part of the sum that is to be minimised will be the same for both.

Fig. 1.



For example, let the segment of the line AC from the point A where it intersects another line, not shown, up to C be a locus of double medians: meaning that if at any point on the locus a line is drawn parallel to  $x$  that point will be the median of the points given by intersection of the said line with the observation-lines, will be an  $x$ -median, say; and will also be a  $y$ -median. Let the line CE be likewise a locus of double medians. And let there be no other double-median points (or loci). The required point then must be on either AC or CE; and it will be on both, at their intersection C. For if it were at any other point on either of the segments, the sum of weighted residuals would be greater by the (weighted) perpendicular let fall from that point on the other line. Now let EF also be a locus of double medians (up to a point where it intersects with another line, not shown). By parity the required point must be either C or E. It will be the intersection of

those two lines for which the weighted perpendicular let fall from the intersection on the third line is the less. Thus if the weights are not very unequal, it will be E, and not C.

Even after the criterion has been applied, there may remain a certain indeterminateness when the condition of least possible sum of residuals is equally fulfilled by all the points on the segment of a line, or even all within an area. In the former case, on the analogy of the practice commonly employed for the simple Median, we should take for the sought point the bisection of the segment which is a double median. In the case of the locus being an area, on the same principle we should take the centre of gravity of the area.

The former case is seemingly not infrequent. For it may be expected that when a line that is the locus of  $x$ -medians crosses a line that is the locus of  $y$ -medians a segment of the  $x$ -median locus will sometimes be also a  $y$ -median. For commonly, where the weights are not very unequal, it is presumable that the number of observation-lines to the right of an  $x$ -median will be nearly the same as that on the left; and likewise the number of lines above a  $y$ -median about the same as the number of those below. Accordingly, it may be expected that, when an  $x$ -median line is intersected by any other line, the  $x$ -median locus after the intersection will be a segment of that second line; the segment which has the first line on the right [or left] after the intersection if before the intersection the second line was on the right [or left] of the first. *Mutatis mutandis*, a like proposition is true of a  $y$ -median. Whence it appears that intersecting median lines will sometimes be so related as to have a segment in common. For example, in fig. 1 if AC is a locus of  $x$ -medians and EF of  $y$ -medians it may be expected that CE will be a locus of both  $x$ - and  $y$ -medians. But if AC [or BC] were an  $x$ -locus and BC [or AC] a  $y$ -locus, then beyond the intersection the loci will continue on different lines, one on CG and the other on CE. Again, if AC is an  $x$ -median and GC a  $y$ -median, CE is probably the continuation of the  $x$ -median, BC of the  $y$ -median; and likewise if  $x$  and  $y$  are interchanged in this statement. If AC is an  $x$ -median and CE a  $y$ -median, or conversely, then it is likely that *both* segments are double medians. In this and the two preceding cases the solution is limited to a point.

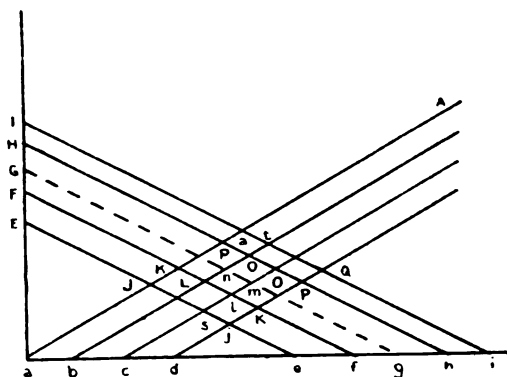
The double-median locus occurs in what is probably the simplest case of the problems under consideration: when the

observation-lines consist of two sets of parallel lines of the respective forms

$$x \cos \alpha + y \sin \alpha - p_r = 0; \quad x \cos \alpha - y \sin \alpha - p_r = 0$$

all of equal worth—there must be at least two sets for the reason given by Laplace: “si la marche de deux éléments [two *quesita* such as our  $x$  and  $y$ ] était rigoureusement la même: ces éléments ne formeraient qu’une seule inconnue” (*Probabilities*, Introduction, ed. 3, § LXIV.). In fig. 2

Fig. 2.



let the number of observations at first be odd; the dotted line  $Gg$  being included. Then the  $x$ -median locus will consist of the following segments:

$$ej, jk, kl, lm, mn, no, op, pq, qI$$

( $ej$  and  $qI$  indefinitely produced at one extremity). Likewise the  $y$ -median locus is

$$EJ, JK, KL, lm, mO, OP, PQ, Qi$$

( $JE$  and  $Qi$  produced indefinitely). The two loci have a common segment  $mn$ ; of which the middle point is to be taken as the solution of the problem.

If, the dotted line  $Gg$  being removed, the number of observations becomes even, each median locus will consist no longer of lines, but of spaces. The  $x$ -median locus will be (1) the space enclosed by the lines  $jd$  and  $je$  produced indefinitely, (2) the quadrilateral  $jkls$ , (3)  $lLoO$ , (4) the quadrilateral  $opqt$ , (5) the space between  $qI$  and  $qA$ . Likewise the  $y$ -locus will consist of spaces; and the two loci will have in common the quadrilateral  $lLoO$  (the dotted line being

absent) of which the central point is to be taken as the solution. This kind of indeterminateness is probably rare; at least as rare as the analogous incident in the case of the single median, a tract of line left vacant (the data being of various weights).

I subjoin some examples illustrative of the preceding statements.

Ex. 1. The first example does not require recourse to first principles. It consists of five equations in which the two sought quantities  $x$  and  $y$  are constants of a curve fitted by Professor Bowley to given statistics ('Journal of Royal Statistical Society,' 1902, pp. 340, 341). Observing several percentiles he connects with intervals, each equal to unity, between successive percentiles the linear function of  $x$  and  $y$  which would be equal to those intervals, theoretically if the series of statistics were indefinitely prolonged. There are thus obtained from the *apparent* percentiles the following five equations:—

$$(b) \ x 0.886 - y 0.1669 = 1,$$

$$(c) \ x 0.635 - y 0.2305 = 1,$$

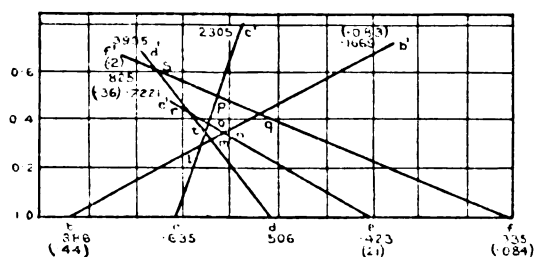
$$(d) \ x 0.506 + y 0.3935 = 1,$$

$$(e) \ x 0.423 + y 0.722 = 1,$$

$$(f) \ x 0.335 + y 0.825 = 1.$$

(In the original there is another equation labelled (a); but as it is of very inferior worth, it is omitted here.) The others are not all of the same worth; but they may be treated as such for a first approximation.

Fig. 3.



The lines representing the equations are drawn in fig. 3 copied from Professor Bowley's fig. (*loc. cit.*). Underneath each line is placed (the numeral not in brackets) the coefficient of  $x$  in the line; and above each line the coefficient of  $y$ . Starting from the axis of  $x$ , let us first find the median

of the five points of intersection on that line. Whereas the sum of all the  $x$ -coefficients is 2.785, the half-sum 1.3925 : since 0.886 is less than the half-sum, and  $0.886 + 0.635$  greater, the point  $c$  is the median. The like is true of every point on the line ( $e$ ) up to  $l$ . At  $l$  the locus of  $x$ -medians changes to  $lm$  : since the  $x$ -coefficient of the only line to the left of  $lm$  is 0.635, less than the half-sum, and this added to 0.886 the coefficient for  $lm$  is greater than the half-sum. By parity, the locus does not turn at  $m$ , but goes on to  $n$ . The series of segments proves to be

$cl, lm, mn, no, op, pc'$  (produced).

Likewise for the  $y$ -medians, whereas the half-sum of the coefficients is 1.169, for a vertical drawn through  $f$  the median is at  $j$  since  $0.1669 + 0.2305$  is less than the half-sum and the same plus the  $y$ -coefficient of the line ( $f$ ) 0.825 is greater than the half-sum. The like is true of every point on that line up to  $q$ . Then the locus changes to  $qn$ . The series of segments is

$jq, qn, no, or, rs, su$  (produced),

$u$  being the intersection of the line ( $e$ ) and ( $f$ ), not shown in the fig. The segment  $no$  being common to the two loci contains the required point ; for which the middle point of the segment may be taken.

Next, let us take account of the fact that the observations are of unequal worth. Roughly ( $c$ ) and ( $d$ ) may be regarded as of equal worth, ( $b$ ) and ( $e$ ) as of only half, and ( $f$ ) as of only a quarter of that worth. The bracketed numerals in the fig. show the altered coefficients. The half-sum of the  $x$ -coefficients is now 0.939 : and accordingly  $c$  is still the median for the axis of  $x$ . The new locus is

$cl, lm, mt, to, op, pc'$  (produced).

Likewise the new  $y$ -locus is

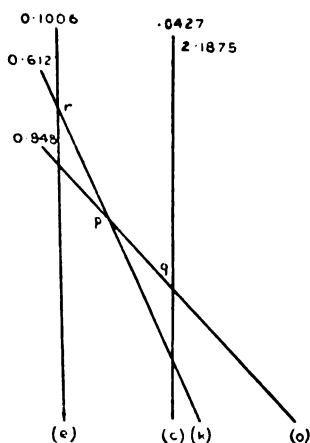
$en, no, ot, tr, re'$  (produced).

The segment  $ot$  common to the two loci affords the solution.

Ex. 2. The next example consists of thirteen equations given by Laplace for the determination of  $x$  (Laplace's " $z$ ") and  $y$ , two constants pertaining to the elliptical figure of the earth (*Mécanique Céleste*, liv. iii., § 41 : two of the fifteen equations there given being here provisionally omitted, as explained presently). The central portion of the network is shown in fig. 4. Whereas the  $x$ -coefficient for all the lines is identical, viz. unity, the  $x$ -median is the locus of points each of which has six lines on the right and six on the left. The lines being labelled ( $a$ ) ( $b$ ) ( $c$ ) . . . . ( $o$ ) in the order of

the intercepts which they make on the abscissa, and the lines (i) and (j) being provisionally omitted, the line (g) forms the  $x$ -median locus in the neighbourhood of the abscissa. Thence, continually turning corners, the locus has come to be, in the neighbourhood represented by the fig.,  $qp$ , a segment of the line designated (o); followed by  $pr$  a segment of the line (k). The designations of the lines are given below, and their  $y$ -coefficients above. The half-sum of all the  $y$ -coefficients being 2·693, the sum of the coefficients for lines above  $pq$  excluding the coefficient of (c)

Fig. 4.



is 2·1875 as indicated on the fig. Accordingly,  $pq$  is a  $y$ -median, since  $2·230 = 2·1875 + 0·0427 < 2·693$ ,  $2·230 + 0·848 > 2·693$ . For a like reason  $pr$  is a  $y$ -median. The two loci do not go together beyond the points  $q$  and  $r$ . Accordingly,  $p$ , the meeting-point of the segments  $pq$  and  $pr$ , is the required determination. Its numerical value will be compared with Laplace's result presently.

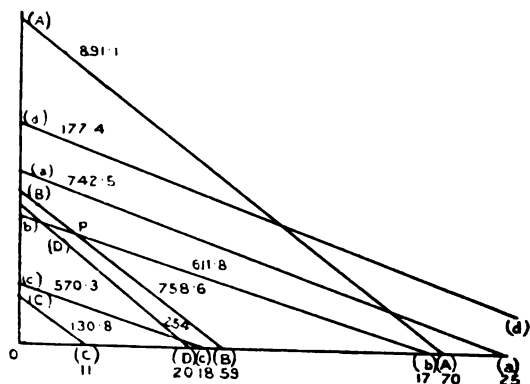
Ex. 3. The next example is formed by eight equations cited by Thackeray in the *Astronomical Monthly Notices*, vol. xvi. p. 335; for two corrections required in the calculation of Venus' semidiameter. The equations are, in the order and with a division given by Thackeray:—

- |                            |                               |
|----------------------------|-------------------------------|
| (a) $25x + 742·5y = 46·27$ | (A) $70x + 891·1y = 112·79$ , |
| (b) $19x + 611·8y = 29·07$ | (B) $59x + 758·6y = 43·91$ ,  |
| (c) $18x + 570·3y = 13·23$ | (C) $11x + 130·8y = 2·71$ ,   |
| (d) $5x + 177·4y = 14·21$  | (D) $20x + 254·3y = 13·87$ .  |



As each of these equations is presumably formed by putting together in different numbers equations of equal worth, the sums as they stand may be taken as representing, by the coefficients, the relative worth of the data. Thus, the sum of the  $x$ -coefficients being 227, the  $x$ -median is the locus of the point which has a sum of  $x$ -coefficients as nearly as may be equal to 113.5 on the right and on the left. Likewise the locus of  $y$ -medians has as nearly as possible coefficients amounting to half 4136.8 above and below. Fig. 5 roughly represents the lines, the unit of  $y$  being ten times larger than that of  $x$ . The  $x$ -coefficients are written below the abscissa (with the exception of line (d)); and the  $y$ -coefficients above

Fig. 5.



each line. Adding up the  $x$ -coefficients from the left we have up to  $b$  exclusive the sum 108 and,  $b$  being included, 127. Thus  $bp$  is part of the  $x$ -median locus. At  $p$ , the point where it meets  $B$ , the locus changes to  $B$ ; the sum on the left exclusive of  $B$  being now  $68 < 113.5$ ; while  $68 + 59 > 113.5$ .

For the  $y$ -median, adding the coefficients from the top downwards along the axis of  $y$ , we have the sum up to  $(B)$  exclusive 1811 and,  $(B)$  being included, 2569.6. Thus the segment of line  $(B)$  above the point  $p$  is a  $y$ -median, as well as an  $x$ -median. At the intersection of  $(B)$  with  $(a)$  the loci part company. Going back to the segment  $pq$  of line  $(b)$ ,  $q$  being the intersection of line  $(b)$  with line  $(A)$  not shown in the fig., we find that it is a  $y$ -median (as well as an  $x$ -median). For the sum of the  $y$ -coefficients above (those of  $(a)$ ,  $(d)$  and  $(A)$ , viz. 1811, is less than the half-sum 2068; while if the coefficient of  $B$ , viz. 611.1, is added, the sum becomes greater than 2068. At  $q$  both loci change to  $(A)$ .

They part company at the next intersection (not shown in the fig.) between (*A*) and (*B*). We have then on the principle above explained to choose between the points *p* and *q*; the choice depending on the question which is the shorter of the two perpendiculars, that from *p* on (*A*) or that from *q* on (*B*), each multiplied by the corresponding weight. In other words, if  $x_1, y_1$  are the coordinates of *p*, and  $x_2, y_2$  those of *q*, the question is which is the smaller,  $70x_1 + 891.1y_1 - 112.79$  or  $59x_2 + 758.6y_2 - 43.9$ . Performing the calculation, I find that the answer is in favour of *q*.

Ex. 4. The next example consists of 29 equations relating to the same corrections as the *x* and *y* of example 3, kindly submitted to me by Professor Turner. The incident that the coefficient is the same, viz. unity, for all the equations (presumably of equal worth) facilitates the tracing of the *x*-median locus (as in Ex. 2). But the selection of the optimum point is embarrassed by the close relation between the two loci, which turn several corners together.

Ex. 5. A still more marked appearance of indeterminateness is presented by an example taken from Laplace's *Mécanique Céleste*, § 41: seven equations involving two constants entering into the elliptical form of the earth as determined by observations on the meridian at different places. When account is taken of the different weight (in the sense above defined, p. 1075), the equations may be written (as they are by Bowditch in a note to his translation)—*x* being here substituted for *z* in the original:—

$$\begin{aligned} 88448.69 - 3.4633x &= 0, \\ 34834.78 - 1.3572x - 0.40928y &= 0, \\ 42072.94 - 1.6435x - 0.65651y &= 0, \\ 61624.50 - 2.4034x - 1.11856y &= 0, \\ 275793.15 - 10.7487x - 5.59932y &= 0, \\ 84071.71 - 3.2734x - 1.79546y &= 0, \\ 27495.85 - 1.0644x - 0.89289y &= 0. \end{aligned}$$

Here the fifth line owing to its preponderance proves to be the median locus both for *x* and *y* throughout. The problem thus becomes: to find the point on that line for which the sum of the weighted perpendiculars on the other lines is the least. We have thus to determine *x* and *y* such that the sum of the left sides in (six of) the above-written equations, each taken in absolute quantity, should be the least possible. But since the point (*x*, *y*) is on the fifth line we may substitute

the value of  $x$  in terms of  $y$  derived from the fifth equation for  $x$  in each of those six equations; and thus we are presented with a problem of the ordinary kind relating to a single median. Performing the requisite operation, I find for  $y$  483.

If this is not in close agreement with Laplace's result, viz. 246.9, it should be remembered that the paucity of the observations and the preponderance of one of them renders the probable error incident to any calculation very considerable. It suffices to observe that the seven values of  $y$  which Laplace finds (by a process described below) range from  $-221$  to  $+1252$ ; and that the weight of one of them is nearly equal to the weight of all the others put together.

The working of the above examples was facilitated by some devices which may be of general application: (1) Whereas it is convenient to transform the coordinates (or one of them) to an origin in the neighbourhood of the sought point, this may often be effected with sufficient accuracy as follows. Distribute the equations into two classes, say, as in Example 3, if the number of the equations was larger, according to the greater or less slope of the lines. Take the medians of the  $x$ -coefficients, of the  $y$ -coefficients, and of the absolute term, for all the equations of the first batch, therewith to construct a derived equation in  $x$  and  $y$ . Likewise from the second batch construct a second derived equation. The two derived equations treated as simultaneous furnish approximate values of  $x$  and  $y$ . (2) Or we may take for the first approximation that point which has as many lines on the right as on the left, and as many above as below. Professor Bowley has with good effect thus treated our example 1 (*loc. cit.*). (3) When the network of lines is much entangled it is convenient to omit some of them provisionally, and to determine an approximate value with the remainder. I thus in Example 2 omitted equations ( $i$ ) and ( $j$ ) which by their proximity threatened entanglement. With the remaining thirteen I found for  $x$  99680.5 and for  $y$  .00551. Transforming to that point as origin, I found for the locus of double medians the segment of a line, the middle point of which is  $x=99679.7$ ,  $y=.00562$ . Which is in satisfactory accord with Laplace's result, viz.  $x=99676$ ,  $y=.00567$ , and the slightly different result which Bowditch, correcting Laplace, I think correctly, substitutes (*loc. cit.*).

The process applied to Example 5 is analogous as to its latter part with Laplace's treatment of the case. But he obtains a first equation whereby to eliminate  $x$  (his  $z$ ), not as a median locus, but by the ordinary method of Least Squares.

In cases like our fourth and fifth this partial use of Least Squares, as well that method in its entirety, has an advantage over our method in respect of what Professor Turner calls "straightforwardness." This advantage is no doubt considerable in the case of several variables, loci to be traced in many-dimensioned space. But the choice of methods cannot be decided without consideration of their relative accuracy. In cases where the method of Medians was known to be much more accurate than that of Least Squares the former might be preferable, even though more laborious as well as less "straightforward."

II. The accuracy of the double Median depends on much the same considerations as those which relate to the single Median. Accordingly, the interest of this second section extends beyond the special object of the article. The comparison of the (single or double) Median method with that of Least Squares is prejudiced by two misapprehensions exaggerating (a) one the defects of the Median, (b) the other the merits of Least Squares

(a) It is presumed that determination by way of Medians is less exact because it sometimes leaves the segment of a line, or even (in the case of the double Median) a space within which no unique value is distinguished. But the comparative definiteness of the Arithmetic Mean is illusory, considering that the determination is liable to a probable error. It has been shown (Phil. Mag. 1888, p. 187) that in the case of the single unweighted Median the tract of line left vacant is likely to be a very small fraction—of the order  $1/\sqrt{n}$ , where  $n$  is the number of equally good observations—of the probable error incident to the Arithmetic Mean. The corresponding proposition for the weighted Median is *à fortiori*. It may likewise be shown that the probability of the vacant tract being as large as the said probable error is extremely small. These propositions may be transferred from the single to the double Median through the proposition that the point, or locus of points, for which the sum of the weighted residuals is the least possible must be an invariant, not varying with the choice of axis. Accordingly, if a large tract of line (or *mutatis mutandis* a space) were left indeterminate, by a proper choice of coordinates, with a point on the tract as origin, the case may be shown to imply the improbability that the Median of numerous (sporadically dispersed) points on a line should be indeterminate over a large tract. The tract of indeterminateness left vacant by the Median may indeed *seem* to be greater than the probable error of the Arithmetic Mean. But that is probably because the probable error of

the Arithmetic Mean is greater than it is represented to be by the usual formula (the square root of the mean square of residuals divided by  $n$  or  $n-1$ , and multiplied by 0.6745). For that formula presumes that the observations are *independent*, uncorrelated, which in the concrete is probably often far from true—for instance, observations of the kind which form our Example 3 (as pointed out by Stone, *Astronom. Monthly Notices*, vol. xxv. p. 57). In short, the Median not only reminds us that our results are liable to a probable error; it may also warn us that the probable error is greater than would commonly be supposed—at least as great as the tract left indeterminate by the Median.

(b) The Method of Least Squares enjoys an undue preference in virtue of its connexion with the Normal Law of Error. For probably that law is not in general fulfilled by observations so perfectly as to justify the preference given. The preferability varies with the character of the observations. I proceed to prescribe one or other of the compared methods for different cases, without knowing in what proportion these cases occur in practice. Three types may be distinguished:

(1) The normal law of error may be fulfilled with the perfection proper to games of chance, and occasionally realized by concrete statistics, *e.g.* measurements of human stature (Yule, 'Theory of Statistics,' ch. xv. § 13). In this case the Arithmetic Mean prescribed by the Method of Least Squares is decidedly preferable on grounds of Inverse Probability. But it should be remembered that even in this case the certain advantage of the Arithmetic Mean is slight; the probable error of the Median is only about 25 per cent. larger than that of the Arithmetic Mean (*cp.* Yule, *op. cit.* ch. xvii. § 3).

(2) Probably a commoner case is where the normal law is fairly well fulfilled by the observations, about as well, say, as in the examples cited by Merriman ('Method of Least Squares,' § 34), by Airy ('Errors-of-Observation,' sub finem), or by Chauvenet ('Astronomy,' vol. ii., Appendix). In this case the advantage of the Arithmetic Mean over the Median is less. It is much less, if, as probable, the imperfection consists of a feature which is specially favourable to the Median, the abnormal protuberance of the extremities of the curve which represents the observations.

(3) When the curve representing the observations is quite abnormal it is very possible that the Median should have the advantage in respect of accuracy. Not that the Method of Least Squares is inapplicable in this case. For—*pace* some distinguished writers—the method, as prescribed by Laplace,

does not demand affinity to the normal form in the distribution of the original crude observations. The normal form which is characteristic of the method is presented not by the crude observations, but by (series of) their *means* (cp. article on "Probability," *op. cit.* § 134-5). But the like is, in general, true of Medians. This kind of *mean*, as well as the Arithmetic, is distributed according to an ancillary normal frequency-curve. Which method is preferable depends on the character of the respective ancillary curves ; which of the two has the smaller modulus (or "standard deviation"). Laplace in his second Supplement has shown cases in which the method of "situation," the single Median, is preferable to the Method of Least Squares. He has recommended the method of situation not only by precept but by example ; having employed it in the determination of constants pertaining to the elliptical form of the earth (*Mécanique Céleste*, liv. iii. § 40, 41). Bowditch, the able translator of the *Mécanique Céleste*, says in a note referring to the passage cited : "This method, proposed by Boscovich, and peculiarly well adapted to the present problem, is not now so much used as it ought to be" . . . . "We shall hereafter find, in several instances, that the method of Least Squares, when applied to a system of observations in which one of the extreme errors is very great does not generally give so correct a result as the method proposed by Boscovich." More generally, when the extremities of the curve representing the crude observations are abnormally protuberant, the Median is apt to be preferable. When very abnormal conditions are apprehended the Median may well be employed to check and control, if not to replace, the ordinary method.

In short, the use of the Median (single or double) is often easier, and sometimes more accurate, than the Method of Least Squares. Nevertheless, the feeling of physicists and mathematical statisticians in favour of the usual practice is no doubt founded not merely on familiarity, but on deeper unexpressed reasons. Some may be suggested. The probable error for the ancillary normal curve pertaining to the Median, depending on the height of the ordinate--the aggregation of the observations--at the centre, is not so readily ascertainable as the corresponding coefficient for the Method of Least Squares. In order that there should exist an ancillary normal curve, it must be postulated that there is an aggregation about the centre ; whereas no such postulate is required for the rival method. The absence of the requisite central aggregation may be serious in a case with which Laplace has introduced the Method of Least Squares

(*op. cit.* liv. ii. ch. 4), and which he has employed with effect—in a manner probably admitting of wide application—to discover laws masked by fortuitous happenings, such as the average difference in the height of the barometer at different times of day (*op. cit.* liv. ii. ch. 5). The case is that in which the crude observations are represented by a rectangle; one value being as likely as another between finite limits—say,  $\pm a$ .

Altogether, we may conclude with Laplace that, in certain cases the Method of Situation is preferable to the Method of Least Squares, the Method called *par excellence* “the most advantageous method” (*op. cit.* Supplement 2, ed. 1847, p. 619); that (in general) it is natural to consider the Median as “a very good approximation” (*op. cit.*, Introduction, p. lxix). “Mais le résultat donné par la méthode la plus avantageuse est encore préférable.”

CXIV. *The Motions of Electrons in Gases and the Formation of Negative Ions in Air.* By LEONARD B. LOEB\*.

**I**N a recent note in this magazine Dr. V. A. Bailey†, in commenting on the writer's work‡ reported in 1921, appears to have been under an erroneous impression as to the method of measurement employed by the writer. In the paper referred to the writer attempted to verify the J. J. Thomson theory of ion formation by studying the mobility curves in air obtained below 10 cm. pressure, using the Rutherford alternating-current method with alternations of *square wave form* obtained from a commutator. This method is the method of experimentation termed by Dr. Bailey the “Lutley modification” of the Rutherford method. Thus the writer did *not* use the method termed by Bailey the “Franck modification,” which involves the use of an alternating current of *sinusoidal* form, as stated in Bailey's note.

In the work quoted above the equations used for a verification of the theory by the writer were but a rough approximation to the rigorous equations, as owing to the uncertain knowledge of many of the factors a greater precision did not seem warranted. The agreement obtained was merely a qualitative one. Lately much more careful measurements have been made, using the *square wave oscillations*, with the added advantage that some rough measurements on the mobilities of electrons in air at the pressures

\* Communicated by the Author.

† Bailey, V. A., *Phil. Mag.* xlv. p. 213 (July 1923).

‡ Loeb, L. B., *Phys. Rev.* n. s. vol. xvii. p. 89 (Feb. 1921).

employed in this work were also made. The results of these investigations, which are shortly to appear in print, enabled the use to be made of the rigorous theory of J. J. Thomson. The results obtained by including the values of the electron mobilities, as measured directly, in the rigorous attachment equations appear to give a striking verification of the theory. When, however, certain corrections which seem theoretically necessary are made on the values of the electron mobilities the agreement initially observed is completely vitiated. In the application of the corrections to the electron mobilities, certain assumptions are made about the space charge effects due to the accumulation of ions which may not be fulfilled in air. Thus it is still doubtful whether the corrected electron mobilities are more justified than the uncorrected ones. It is therefore, at present, an open question whether the *rigorous form* of the Thomson theory is correct or not.

The writer agrees with Dr. Bailey that it is possible that " $h$ ," the attachment constant of J. J. Thomson, may decrease as the velocity of thermal agitation " $u$ " decreases, though he is unaware of any direct evidence that this is so. He desires to point out that for the change in " $u$ " produced by *higher* fields H. B. Wahlin \* found no evidence of a marked change in " $h$ ." It is also desired to point out that in order of magnitude " $h$ " is such a distinct function of the chemical nature of the gas that even were the assumption of Bailey correct (viz., that " $h$ " is a function of " $u$ "), the theory of Thomson would be applicable in its broad outlines.

The writer has unfortunately long been aware of the fact that the use of sinusoidal alternating potentials of high frequency for the measurement of electron mobilities is an unsatisfactory mode of procedure. Yet up to the present the method has furnished the only means of estimating the electron mobilities in most gases above 100 mm. pressure. It might be pointed out that where the results obtained by the writer using sinusoidal oscillations overlap the very beautiful results of Townsend, Bailey, and their collaborators, they are roughly in agreement with them, as will be seen in a forthcoming paper by K. T. Compton †.

Department of Physics,  
University of California,  
Berkeley, Calif.  
Aug. 25, 1923.

\* Wahlin, H. B., Phys. Rev. n. s. vol. xix. p. 173 (Feb. 1922).

† Compton, K. T., "Mobilities of Electrons in Gases," Phys. Rev. n. s. vol. xxii. (1923) (to appear).



CXV. *On the Motion of Electrons in Gases.*

*To the Editors of the Philosophical Magazine.*

GENTLEMEN,—

I HAVE received a letter from Dr. L. B. Loeb with which he encloses a copy of a note he has sent to the *Philosophical Magazine*, taking exception to a statement I made on his work in connexion with the formation of negative ions and the measurements of the velocities of electrons in gases.

My statement consisted of seven lines, and as Dr. Loeb has written several papers on these subjects, no reader would suppose that I had related all Dr. Loeb's work. The main facts to which I alluded, however, are those published by him in the *Philosophical Magazine* of January 1922, and in my paper I gave that reference.

In his paper of January 1922 Dr. Loeb gives reasons which led him to suppose that previous determinations of "mobilities" were unreliable, and states that in his latest experiments on the determination of the mobility he used "*high-frequency oscillations from an audion oscillator.*" He thus obtained a value of the "mobility" which was 2800 cm./sec. for nitrogen, which he points out is much higher than the value 200 cm./sec. given by other experimenters, and he adopts the higher number as the fundamental basis of the calculations of the chance of ion formation which he gives in this paper.

Under these conditions I am surprised to find the following sentence in Dr. Loeb's note to the *Philosophical Magazine*: "Thus the writer did *not* use the method termed by Bailey the 'Franck modification,' which involves the use of an alternating current of *sinusoidal* form, as stated in Bailey's note," as the high-frequency oscillations from an audion oscillator are usually supposed to be of sinusoidal form.

I have therefore looked up another paper by Dr. Loeb (*Physical Review*, p. 24, 1922) where he gives a diagram and full details of his experiments with the audion oscillator, and it is clear from this paper that the apparatus is designed to generate oscillations of sinusoidal form, and they are treated as such in the investigation.

Dr. Loeb appears not to have noticed the fact that I referred to his paper in the *Philosophical Magazine* of January 1922, where he gives the impression that "mobilities" determined by sinusoidal alternating forces are reliable.

The statement in Dr. Loeb's note that the method of determining electron "mobilities" by means of sinusoidal alternating potentials has up to the present "furnished the only means of estimating electron mobilities in most gases above 100 mm. pressure," is by no means correct. Townsend's method, involving the magnetic deflexion of a stream of electrons moving in a uniform electric field, may be used to determine the velocity of electrons in a gas at any pressure when no ions are present. Most of the determinations, it is true, have been made with gases at pressures below 100 mm., because the smaller the pressure the smaller is the magnetic force required to deflect the stream, and it is easier to work with small magnetic forces than with large forces involving the use of coils with iron cores. From the measurements that have been made it has been found that the velocity in the direction of an electric force  $Z$  is a function of the ratio  $Z/p$ , so that if the velocities are determined for one value of  $Z$  and one value of  $p$ , they may be considered as being known for any multiples  $nZ$  and  $np$  of this force and pressure.

Yours truly,

V. A. BAILEY.

Electrical Laboratory,  
Parks Road, Oxford.  
Sept. 13, 1923.

CXVI. *On Atomic Structure and the Reflexion of X-Rays by Crystals.* By D. R. HARTREE, B.A., *St. John's College, Cambridge* \*.

### § 1. *Introduction.*

**I**N a recent paper † I have given an account of an attempt to determine approximately the field inside and in the neighbourhood of an atom by quantitative analysis of the terms appearing in the optical and X-ray spectra, following the theory given in a more qualitative form by Bohr. It was pointed out there that the dimensions of the orbits and variation of time along them could be calculated approximately from the results of this analysis and applied to the problem of the intensity of the reflexion of X-rays by crystals, and some preliminary results of this application to sodium were quoted and compared with Bragg's experimental results ‡.

\* Communicated by R. H. Fowler, M.A.

† D. R. Hartree, *Proc. Camb. Phil. Soc.* vol. xxi. part 6 (1923).

‡ W. L. Bragg, R. W. James, and C. H. Bosanquet, *Phil. Mag.* xli. p. 309; xlii. p. 1 (1921); xlii. p. 433 (1922). These papers will be referred to as B. J. B. i, ii, and iii.

The object of the present paper is to consider this application in more detail, and also to inquire whether and to what extent it may be possible to obtain from X-ray reflexion evidence on the orientations of the orbits in the atom and on the relative phases of the electrons in the different orbits

For simplicity we will consider a rocksalt crystal, as it is for rocksalt that the experimental work has been done, and it is quite sufficient for the purpose of this paper. With the arrangement of atoms in the rocksalt crystal, the different possible reflecting faces can be divided into two groups: namely, those for which every plane of atoms parallel to the reflecting face is similarly constituted, *i.e.*, contains equal numbers of Na and Cl atoms regularly arranged, and those for which alternate planes are differently constituted, *i.e.*, contain Na atoms only and Cl atoms only. The former are faces for which one index is even, the latter those for which all indexes are odd; they will be referred to as "even" and "odd" faces respectively.

The formula for the intensity of X-ray reflexion need not be quoted here in its entirety. The important part of it for the purposes of this paper is the factor, written  $F^2$  in Bragg's papers, which depends on the number and arrangement of electrons in each scattering atom. If the wavelets scattered by the individual electrons are all in phase, then  $F$  is equal to the number of electrons concerned in the scattering; this is the case when the electrons are distributed in a space small compared with the wave-length of the incident X-rays, and also in certain other conditions. When the wave-length of the incident X-rays is of the same order as the distances between the various electrons, the scattered wavelets are not in general all in phase, and the amplitude of the wave scattered by the atom as a whole will be less than that scattered when the wavelets are in phase; this is expressed by a smaller value of  $F$ . The extent of this interference depends on the electron arrangement and on the angle of scattering.

The scattering by the individual electrons is assumed to be properly deduced from classical electrodynamics; the results so obtained are at any rate of the right order, as pointed out in Bragg's paper\*. The amplitude of the wavelet scattered by one electron according to classical electrodynamics will be taken as the unit of amplitude; the value of this unit in terms of the mass and charge of the electron etc., and also the summation of the contributions

\* B. J. B. iii. p. 446.

from the whole of the crystal, is taken into account in the coefficient of  $F^2$ ; we are here concerned only with the pure number  $F$  which is the property of a single atom or a mean property of the atoms.

We will consider the incident wave to be plane, and the interference to be taking place at infinity. The wave reflected from the whole crystal is the resultant of the waves reflected from each plane of atoms in the crystal parallel to the reflecting face; if the reflexion conditions are satisfied then all the waves reflected from similar planes are in phase and those reflected from different planes have definite phase relations. Moreover, each wave reflected from a plane is made up of the waves scattered by each atom.

If any one electron is situated at a distance  $x$  from the plane parallel to the reflecting plane, containing the centre of the atom to which it belongs, then the wavelet scattered by it for glancing angle  $\beta$  differs in phase by  $(4\pi x \sin \beta)/\lambda$  from that scattered by an electron in the plane  $x=0$ , which is conveniently taken as zero of phase. The summation of the effects of the wavelets scattered from different electrons is best done by means of the complex variable; since the amplitude of the wavelet due to one electron is taken as unity and the phase difference from standard is  $(4\pi x \sin \beta)/\lambda$ , then if

$$z = \Sigma \exp [(4\pi i x \sin \beta)/\lambda], \quad . \quad . \quad . \quad (1.1)$$

$|z|$  is the amplitude and  $\arg z$  is the phase of the resultant vibration, the summation being taken over all relevant electrons. Similarly for a distributed charge, if  $de$  is the charge lying between planes  $x$  and  $x+dx$ ,

$$z = \int \exp [(4\pi i x \sin \beta)/\lambda] de. \quad . \quad . \quad . \quad (1.2)$$

We will first calculate  $F$  for a model atom in which the actual moving distribution of electrons has been averaged out into a spherically symmetrical distribution of charge (§ 2), and then for an atom in which the plane of the orbit of each electron is supposed to be fixed, but the electron distribution is averaged out in the plane of each orbit (§ 3). We will then show under what conditions this averaging process is justified (§ 4), and evaluate  $F$  for an atom model which is less simple than either of those considered in § 2 and § 3, but is probably a nearer approximation to reality (§ 5). A short review of the experimental results (§ 6) is followed by a consideration of the numerical results obtained from the use of the formulae established in §§ 2-5 (§ 7).

§ 2. *Spherically Symmetrical Atoms.*

We will consider first an atom in which each orbit has been averaged out into a spherically symmetrical distribution of charge.

A circular orbit radius  $r$  will average out into a uniformly charged spherical shell of the same radius with total charge 1, and the contribution to  $F$  is  $(\sin \xi)/\xi$  per electron \*, where

$$\xi = (4\pi r \sin \beta)/\lambda, \quad \dots \dots \dots (2.1)$$

$\lambda$  being the wave-length of the X-rays and  $\beta$  the glancing angle.

If the electron in a non-circular orbit spends a fraction  $df$  of the radial period between  $r$  and  $r+dr$ , then this orbit averages out into a spherically symmetrical volume distribution in which the charge enclosed between radius  $r$  and  $r+dr$  is  $df$ . The contribution of this shell to  $F$  is  $(\sin \xi/\xi) df$  where  $\xi$  is given by the above formula, and as the waves scattered by all the shells are obviously in phase, the total contribution of a non-circular orbit is  $\int (\sin \xi/\xi) df$ , so altogether

$$F = \sum \int \frac{\sin \xi}{\xi} df, \quad \dots \dots \dots (2.2)$$

the summation being taken over all orbits †.

If, as for the even faces of rock-salt, each reflecting plane contains equal numbers of the two kinds of atoms, then, since the waves from each kind of atom must be in phase, the values of  $F$  can be added directly; and if the molecule and not the atom is taken as the unit of structure the value of  $F$  to use in the reflexion formula is the sum of the values of  $F$  for the separate atoms. Obviously for spherically symmetrical atoms  $F$  is a function of the angle of reflexion only and does not depend on the face from which reflexion takes place.

§ 3. *Planes of Orbits Fixed.*

We will next consider a less drastic process of averaging, and treat the planes of orbits as fixed. The circular orbit then averages out into a ring distribution of charge. If  $\phi$  is the angle between the normal to the plane of the orbit and the normal to the reflecting face, and  $r, \theta$  are polar coordinates on the plane of the orbit, then  $x = r \cos \theta \sin \phi$ ;

\* See B. J. B. iii, p. 439.

† For a circular orbit  $r$  and hence  $\xi$  is constant over the whole orbit, and  $\int df = 1$ .

also in formula (1.2),  $d\epsilon = d\theta/2\pi$ , for the ring is uniformly charged and carries a total charge of unity.

Hence putting as before

$$(4\pi r \sin \beta)/\lambda = \xi,$$

we have

$$\begin{aligned} z &= \int_0^{2\pi} \exp [(4\pi i r \cos \theta \sin \phi \sin \beta)/\lambda] d\theta / 2\pi \\ &= \int_0^{2\pi} \exp (i\xi \cos \theta \sin \phi) d\theta / 2\pi = J_0(\xi \sin \phi). \quad (3.1) \end{aligned}$$

Since the non-circular orbits are multiply and not singly periodic, they average out to a sheet of charge symmetrical about the nucleus, and it is easy to see that the contribution given by such a sheet is

$$z = \oint J_0(\xi \sin \phi) df, \quad (3.2)$$

where as before  $df$  is the fraction of a period spent by an electron between  $r$  and  $r + dr$ .

Since the contributions from all electrons are in phase (for  $z$  is purely real for them all),

$$F = \Sigma \oint J_0(\xi \sin \phi) df, \quad (3.3)$$

and, as for the spherically symmetrical atom, the values of  $F$  are to be added numerically if each reflecting plane is similarly constituted and contains more than one kind of atom.

#### § 4. Justification of Averaging Process.

We must now consider what may happen in actual fact : obviously each atom is not actually spherically symmetrical at each instant, and even if the mean distribution of the electrons in the atom over the lapse of a long time does give a spherically symmetrical distribution of charge, it is not justifiable to average out the electron distribution first and then calculate the reflected intensity ; the instantaneous reflected intensity should be calculated and then averaged with respect to time.

It is fairly obvious that if we are going to consider the instantaneous reflected intensity we can no longer assume that the atoms of the same kind all have the same spatial distribution of electrons. Even if the motions of the electrons in a given orbit \* were the same and in phase for all atoms,

\* I. e. in an orbit specified by given quantum numbers.

a given wave reaches different atoms at different times and so would be scattered differently by each atom; actually there seems no reason to imagine any necessary relation between the phases of the electrons in different atoms, though such relations almost certainly exist between the electrons in a single atom.

Now consider all the atoms of one kind in one single reflecting plane, and for each atom consider the electron in some given circular orbit. Since the only coordinate which occurs in the formulae is the perpendicular distance from the electron to the plane of nuclei, we can consider all the atoms moved in the plane till their nuclei are coincident. Then, if the electron is equally likely to be in any direction from the nucleus, the result will be a uniform spherical shell of charge, since the number of atoms in each plane is very large. This shell can then be divided up again into a series of uniform shells each with a total charge unity, one to each atom. Hence the unjustifiable averaging with respect to time for a single atom has been replaced by a valid averaging at each instant of time over all atoms of the same kind in each reflecting plane.

Similar considerations apply to the non-circular orbit.

If the plane of the orbit is supposed fixed with respect to the crystal, then a similar averaging over all atoms of the same kind in one reflecting plane gives the uniform ring distribution of charge for the circular orbit, as considered in § 3.

In § 3 use had to be made of the property of the non-circular orbit that it was multiply periodic, in order that it should average out into a sheet with circular symmetry. It is now only necessary to suppose that the directions of the axes of the instantaneous ellipses of the motions of the electrons in the different atoms are distributed at random in the plane of the orbit at any instant. It is possible that this might not be the case if the orbits were simply periodic.

As a partial confirmation of the argument it is interesting to take the results obtained by assuming the plane of the orbits fixed, and then average over all possible orientations of the plane, each direction being equally likely, so that the points in which the normal to the plane cuts the unit sphere cover it equally densely all over; the results should of course be the same as for spherical distribution. It is sufficient to consider a circular orbit for which, when the plane of the orbit is fixed,

$$z = J_0(\xi \sin \phi). \quad . \quad . \quad . \quad . \quad . \quad (3.1)$$

The area of the unit sphere between  $\phi$  and  $\phi + d\phi$  is  $\sin \phi d\phi$ , so the averaging over all possible directions of the normal gives

$$z = \int_0^{\pi/2} J_0(\xi \sin \phi) \sin \phi d\phi \quad (4.1)$$

Putting  $m=0, n=-\frac{1}{2}$  in the general formula \*

$$J_{m+n+1}(x) = \frac{x^{n+1}}{2^n \Gamma(n+1)} \int_0^{\pi/2} J_m(x \sin \phi) \sin^{m+1} \phi \cos^{2n+1} \phi d\phi,$$

and substituting in (4.1), we have

$$z = (\pi/2\xi)^{\frac{1}{2}} J_{\frac{1}{2}}(\xi) = (\sin \xi)/\xi,$$

agreeing with the result of § 2.

So the calculation for the spherically symmetrical atom can be carried out in two steps, first averaging over all possible positions of the electron in a given plane of the orbit, and then over all possible planes. The importance of this division is that the second averaging can now be restricted and not taken uniformly over the whole sphere. This will be considered in the next section. Meanwhile it should be mentioned that only for the spherically symmetrical atom is  $F$  independent of the crystal face, and it is only in such a case that the method used by Bragg to separate the effects of the two kinds of atoms in rocksalt is valid.

### § 5. Atom with Planes of Orbits restricted but not fixed.

As has just been shown, if we imagine the direction of the normal to the plane of a given orbit in the various atoms of one kind to be entirely at random, then the crystal reflects as if each atom were spherically symmetrical, and the reflexion can be calculated for this case, and also for the case when the normal to a given orbit is supposed fixed in the crystal.

We must now consider a little more closely the structure of the atom and of the crystal, and see if there is any reason to expect the normal to the plane of a given orbit to be unrestricted or restricted, and in the latter case what sort of restriction to expect.

There are two separate points involved—the possible orientation of the orbits in a single atom with respect to some axis in that atom, and the possible orientation of this

\* See G. N. Watson, 'A Treatise on the Theory of Bessel Functions,' (Camb. Univ. Press, 1922) p. 373.



axis with respect to the crystal axis. If either of these orientations is unrestricted the crystal will reflect accurately as if each atom were spherically symmetrical. It will probably be accepted that in each atom the orbits are definitely orientated with respect to some axis; the question is rather, are the directions of these atomic axes distributed at random or are they restricted?

If the axis of each atom is restricted in direction at all, the most reasonable thing is to expect it to be parallel to one of the crystal axes, but as there is no difference between the six faces of an ordinary cubic crystal, for example, the directions of the atomic axes must be distributed equally among the two senses of the three crystal axes.

Turning now to the orientations of the orbits with respect to the axis of the atom, Bohr\* considers that in a group of four electrons of the same total and azimuthal quantum numbers (such as occurs in Na and Cl), the instantaneous planes of the four orbits are arranged parallel to the sides of a tetrahedron which is definitely not regular and only has one axis of symmetry, which is aligned along the axis of the atom. If this tetrahedron were regular there would be no unique axis about which rotation would be likely to occur rather than about any other, and it might be expected to set itself with its dyad axes (which are mutually perpendicular) parallel to the crystal axes. But as the tetrahedron is deformed so as to have only one axis of symmetry, it may be expected to be capable of rotation as a whole about this axis; or, what is more important from the present point of view, it may be considered that for different atoms the azimuth of the tetrahedron about the axis of symmetry is unrestricted. Then averaging over all atoms whose axes are parallel to a given crystal axis, a circular orbit averages out into a distribution of charge which is best described as that due to a uniform ring of charge rotated about the axis of the atom.

To calculate the scattering by this distribution of charge, let  $\phi_0$  be the (fixed) angle between the normal to the plane of a given circular orbit of radius  $r$  and the axis of an atom. Take the crystal axes as axes of  $x, y, z$ , and let the axis of the atom be parallel to the  $x$  axis. Then the ring of charge must be supposed to be equally likely to be in any azimuth about this axis. Let  $l, m, n$  be the direction cosines of the normal to the face of the crystal; then it is easy to see that for a given azimuth  $\psi$  of the ring, the angle  $\phi_1$  between the

\* N. Bohr, 'The Theory of Spectra and Atomic Constitution' (Camb. Univ. Press, 1922) pp. 93, 95.

normal to the ring and the normal to the crystal face is given by

$$\cos \phi_1 = l \cos \phi_0 + m \sin \phi_0 \sin \psi + n \sin \phi_0 \cos \psi, \quad (5.1)$$

while by §3 the contribution of this ring at this azimuth to the scattering is

$$z = J_0(\xi \sin \phi_1), \quad . \quad . \quad . \quad . \quad . \quad . \quad (3.1)$$

$$\xi = (4\pi r \sin \beta)/\lambda \quad . \quad . \quad . \quad . \quad . \quad . \quad (2.1)$$

As the ring is to be rotated uniformly about the axis of  $x$ , *i. e.*  $\psi$  is equally likely to have all values between 0 and  $2\pi$ , we obtain as the mean contribution of the given orbit from the atoms which have their axes parallel to the  $x$  axis,

$$z = \int_0^{2\pi} J_0(\xi \sin \phi_1) d\psi / 2\pi.$$

Since the atoms are considered to have their axes distributed equally along the three crystal axes, the mean contribution of a given orbit to  $F$ , over all the atoms of the same kind, is

$$z = \int_0^{2\pi} \frac{1}{3} [J_0(\xi \sin \phi_1) + J_0(\xi \sin \phi_2) + J_0(\xi \sin \phi_3)] d\psi / 2\pi \\ = I_{\alpha\beta\gamma}(\xi), \quad . \quad . \quad . \quad . \quad (5.2)$$

where  $\cos \phi_2, \cos \phi_3$  are obtained from (5.1) by cyclical interchange of  $l, m, n$ . Obviously  $I$  will depend on  $l, m, n$ , *i. e.* on the face of the crystal from which reflexion is taking place; it is convenient to take the indices  $\alpha, \beta, \gamma$  of the face as suffixes to  $I$ , as they are integers while  $l, m, n$  are generally irrational. We have of course

$$l, m, n = \frac{\alpha, \beta, \gamma}{(x^2 + \beta^2 + \gamma^2)^{1/2}} \quad . \quad . \quad . \quad . \quad (5.3)$$

For the whole atom the value of  $F$  becomes

$$F_{\alpha\beta\gamma} = \sum_j \int_0^1 I_{\alpha\beta\gamma}(\xi) df, \quad . \quad . \quad . \quad . \quad (5.4)$$

where as before  $df$  is the fraction of a period which the electron spends between radii  $r$  and  $r + dr$ , and  $\xi = (4\pi r \sin \beta)/\lambda$ .

It is more convenient to deal with the spherical model as standard and work in terms of deviations from it; for this purpose we define a new function

$$\Delta_{\alpha\beta\gamma}(\xi) = I_{\alpha\beta\gamma}(\xi) - \frac{\sin \xi}{\xi}, \quad . \quad . \quad . \quad . \quad (5.5)$$

so that

$$F_{\alpha\beta\gamma} - F_0 = \sum_j \int_0^1 \Delta_{\alpha\beta\gamma}(\xi) df, \quad . \quad . \quad . \quad . \quad (5.6)$$

where  $F_0$  is the value of  $F$  calculated for a spherical atom.

On expanding the Bessel functions in (5.2) and performing the integration with respect to  $\psi$ , it appears that the term in  $\xi^2$  in  $\bar{I}$  is independent of  $\phi_0$  and of  $l, m, n$ , and moreover it disappears entirely when  $(-\sin \xi)/\xi$  is subtracted from  $\bar{I}$ , so that  $\Delta$  is fourth order in  $\xi$  at the origin. This is one reason why it is so convenient to work with.

Expanding further we find

$$\Delta_{\alpha\beta\gamma}(\xi) = \frac{\xi^4}{192} g(\phi_0) \left[ \frac{\alpha^4 + \beta^4 + \gamma^4}{(\alpha^2 + \beta^2 + \gamma^2)^2} - \frac{3}{5} \right] + O(\xi^6) \quad (5.7)$$

where

$$g(\phi_0) = 1 - 5 \sin^2 \phi_0 + \frac{35}{8} \sin^4 \phi_0.$$

This shows the order of magnitude of the difference between the values of  $F$  for different faces for small glancing angles. It cannot be used for quantitative comparison with experiment, as higher order terms become appreciable, in the case of the outer orbits of the chlorine atom, for values of  $\xi$  not much greater than the minimum available value\* for NaCl. Higher order terms rapidly become very complicated, and actually it is easier to evaluate  $\bar{I}$  and  $\Delta$  by numerical integration than from the series. However, from this formula we can obtain some rough information about the difference between the different faces of the crystal. The maximum and minimum values of  $l^4 + m^4 + n^4$ , subject to the restriction  $l^2 + m^2 + n^2 = 1$ , are given by  $l^2 = 1, m = 0, n = 0$  (or a cyclical interchange of the three letters), and  $l = m = n$ . These correspond to the crystal faces (100) and (111) respectively, so the intensities reflected from these two faces, which are the most important ones in practice, will be the furthest removed from that due to a symmetrical atom, and in opposite directions; whether even so the difference is appreciable can only be settled by numerical evaluation of  $\Delta$ .

The separation of the fourth order term in  $\Delta$  into factors, one depending on  $\phi_0$  only and the other on the indices of the face only, appeared at first sight as pure accident, but it can be shown to be necessary. Obviously the integral of  $\Delta$  over values of  $l, m, n$  corresponding to a uniform covering of the unit sphere must vanish identically; but for the fourth order term  $l, m, n$  can only appear in the combination  $l^4 + m^4 + n^4$ , whose average value over the sphere is  $3/5$ . A similar simplification does not occur in higher order terms, as  $l, m, n$  can occur in more than one combination.

\* See § 8.

§ 6. *Experimental Results.*

The experimental results suitable for comparison with the formulæ deduced above are those of Bragg, James, and Bosanquet\* on the reflexion of X-rays by rocksalt. There are really two points to be investigated: the relative intensities of the beam reflected from different faces, and the absolute intensities. The first point is only considered rather briefly in the papers referred to. But if the intensity of reflexion actually depends on the face from which reflexion takes place, as well as on the glancing angle, the effect is worth investigation for two reasons at least:—

1. It may give information about the orientation of orbits in the atom or of atoms in the crystal;
2. It vitiates the method used to separate the effects of the two kinds of atoms;

so it seemed worth while to look into the matter more closely.

For this purpose Bragg's original uncorrected results were taken, and  $A \sin \beta$  plotted against  $\sin \beta$ , where  $A^2$  is the observed intensity relative to the (100) reflexion, and  $\beta$  is the glancing angle as before. The object of plotting  $A \sin \beta$  instead of  $A$  is that it is more nearly constant, and it seemed probable that this plot would be one of the most sensitive to the effect that was being looked for.

The results are shown in fig. 1; the figures by each plotted point indicate the order of the reflexion and the face from which it takes place, following Bragg's convention of multiplying the indices of the crystal face by  $m$  for an  $m$ th order reflexion, *e.g.* (333) indicates a third order reflexion from the (111) face.

For high intensity reflexions the mechanical nature† of the crystal face has a very large effect on the intensity of reflexion, so not much weight must be given to the apparent differences between the faces shown by the (100) (110) and (222) reflexions; but for larger glancing angles the effect is small, and here there is at least a suggestion of a difference between different faces: taking the (100) face as standard, the points for the (330) and (444) reflexions are high by an amount of the order of 15 per cent. or of 30 per cent. in observed intensity. On the other hand, the point for the (220) reflexion agrees with the curve for the (100) face. Also for the odd faces the point for the (311) reflexion appears to be low. On the whole it seems that the results may be significant as regards differences between faces, but cannot be considered certainly so.

\* B. J. B. i and ii.

† This term is meant to denote the state of the crystal face in regard to such properties as degree of polish, warping of the crystal planes, etc.

Figs. 1 and 2.— $A \sin \beta$  plotted against  $\sin \beta$ , where  
 $\beta$  = glancing angle,  
 $A^2$  = reflected intensity relative to (100) face.

Fig. 1.

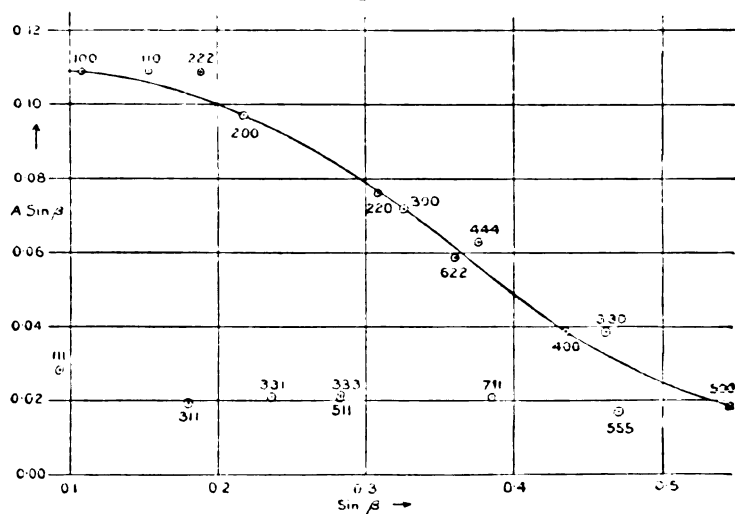


Fig. 2.

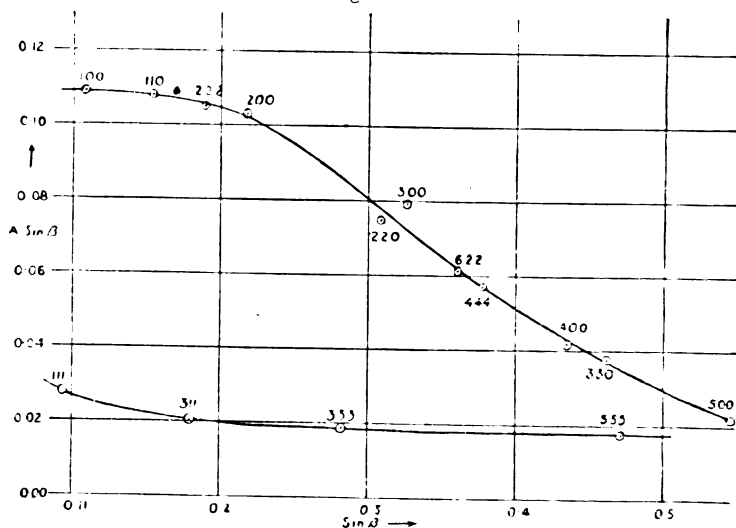


Fig. 1.  $A^2$  taken direct from Bragg's original results.

The curve for even faces is drawn through the points for the (100) face. No curve is drawn for the odd faces as the number of points for any one face is not sufficient to define a significant curve.

Fig. 2.  $A^2$  corrected for 'face effect' (§7.2).

Points for different faces have been given equal weight in drawing the curves.

It appears probable that the Debye correcting factor is a function of the glancing angle only, and does not depend on the face, or only slightly, and the same may be true of the extinction correction, so it does not seem that these two effects would alter the conclusion suggested by the last paragraph, that the intensity of reflexion may actually depend on the face from which reflexion takes place as well as on the glancing angle.

The absolute values of  $F$  given by Bragg are affected by uncertainty about the mechanical nature of the crystal face, and also about the real form of the correction for heat motion, more seriously than the relative values for different faces: the former uncertainty is serious at small glancing angles and the latter at large. There is now also the further doubt of the method used to separate the effects of the two atoms.

### § 7. *Numerical Results.*

The dimensions of the orbits and variation of time along them, which are necessary in order to make a quantitative comparison of theoretical with experimental results, have been obtained by analysis of the terms of the optical and X-ray spectra in the way already mentioned. For Na the atomic field so determined has been used directly, for Cl the field was extrapolated from those of K and Ca, and then adjusted to the X-ray spectrum of Cl; the calculated orbits must therefore be considered as less reliable than those for Na; the doubt is principally concerned with the outer part of the atom.

In figs. 3 and 4  $\frac{df}{dr}$  is plotted as a function of  $r$  for the non-circular orbits of the ions of Na and Cl as calculated in this way. The radii of the circular orbits are also shown. This function is all that is necessary for the calculation of the X-ray reflexion; the actual orbit is not required.

#### § 7. 1. *Atomic Radii.*

Before going on to the intensity of X-ray reflexion by crystals, it is interesting to compare the dimensions of the atoms as calculated by the above methods with the values of the "radius of the atom" deduced by Bragg from the packing of the atoms in crystals\*. For electropositive elements these values are only upper limits for the radius of the outer group of electrons present (on Langmuir's theory), which corresponds roughly to the radius of the smallest

\* W. L. Bragg, *Phil. Mag.* xl, p. 169 (1920).

Figs. 3 and 4.—Calculated curves of  $\frac{df}{dr}$  for X-ray orbits of Na and Cl.

$df$  = fraction of a complete period spent by an electron between  $r$  and  $r+dr$ .

Unit of  $r$  is the radius of the  $1_1$  orbit of the hydrogen atom (0.532 A.U.).

Calculated radii of circular orbits are shown by short vertical lines cutting the axis of  $r$ .

Fig. 3.

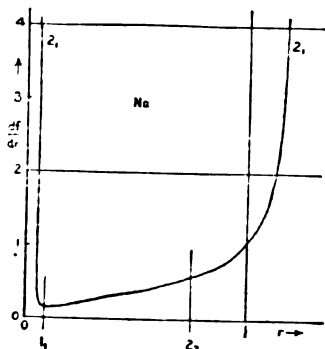
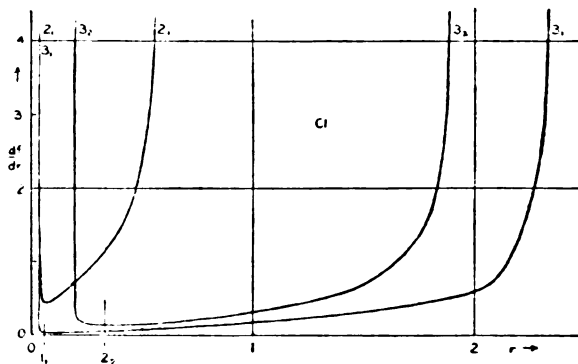


Fig. 4.



sphere enclosing all orbits of the ion (on Bohr's theory). For the electronegative elements Bragg's values are probably slightly low estimates for this radius, and for the inert gases \* approximately correct estimates.

For Na, Bragg's value is 1.8 A.U., for Ne 0.65 A.U. The maximum calculated radius for the Na ion is that of the  $2_1$  orbit, and is 0.65 A.U., this is smaller than Bragg's upper

\* Obtained by extrapolation from the preceding electronegative elements.

limit and just the same as his value for Ne; the actual radius of the ion would be expected to be slightly smaller for Na than for Ne, but the agreement is surprisingly good considering the entirely different means of obtaining the estimates. The maximum calculated radius of the  $3_1$  orbit, the normal orbit of the valency electron, is 2.6 A.U.; this is greater than Bragg's upper limit and suggests very strongly (apart from other evidence) that the atom is ionized, for the normal  $3_1$  orbit would penetrate well into the Cl atom in rocksalt. If the Na atom is not ionized, the  $3_1$  orbit must be profoundly modified, and it is assumed in all calculations to follow that the atoms are present as ions.

For Cl, Bragg's value from the packing in crystals is 1.06 A.U., the maximum calculated radius of an orbit normally present in an ion is 1.22 A.U.; considering the extrapolation required to obtain the latter value, its agreement with Bragg's cannot be considered bad, especially as his value is probably rather an underestimate.

### § 7.2. Differences between Faces.

In order to obtain numerical estimates of the differences between different faces it is necessary to specify the value of  $\phi_0$ , the angle between the normal to the plane of an orbit and the atom axis, for each orbit. As already mentioned, Bohr considers that the four orbits of the same quantum number are arranged parallel to the sides of a tetrahedron with one axis of symmetry which is aligned parallel to the axis of the atom. Since the amount and even the direction of the distortion from a regular tetrahedron is unknown, the tetrahedron will be taken as regular with a dyad axis parallel to the crystal axis, the object of the distortion being simply to define an unique axis about which the tetrahedron is considered to be capable of rotation. Then  $\sin^2 \phi_0 = 2/3$  for all orbits occurring in groups of four with the same quantum numbers. On account of the high order of zero of the  $\Delta$  functions at the origin, the K orbits contribute nothing appreciable to the difference from a spherically symmetrical atom, and so the value of  $\sin \phi_0$  for them need not be specified.

The values of the  $\Delta$  functions for the (100) (110) (111) and (311) faces are shown in fig. 5. It will be seen that the difference between any pair of these four faces remains constant in sign till  $\xi$  is greater than 7, which is just about the maximum value it takes in the case of the sodium atom, with values of the glancing angles used in the experiments.

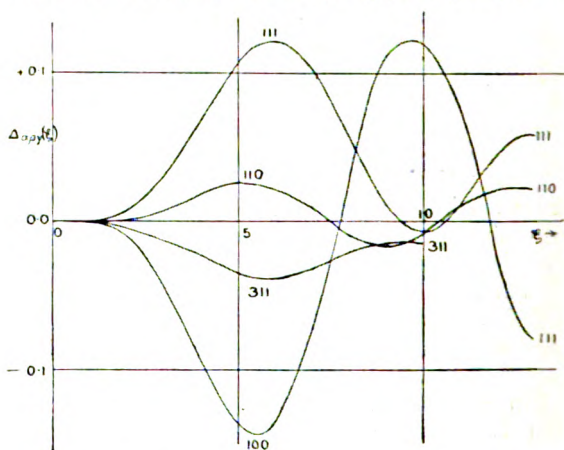


So that the contribution of the Na atoms has always the sign of the first term in the expansion for  $\Delta$ .

From the dimensions of the orbits and the  $\Delta$  functions, the differences of the values of  $F$  for different faces can be calculated; some figures are given in § 7.3. From these, rough corrections to the original observations can be obtained. To avoid as far as possible the difficulties connected with extinction and the Debye correction for heat motion, the correction was applied as follows. The factor necessary to reduce the theoretical results for a face to those for spherically symmetrical atoms was calculated for each face

Fig. 5.

Curves of  $\Delta$  functions for faces (100), (110), (111), (311).



for a series of glancing angles and plotted, and each value of  $A$  [the square root of the observed intensity relative to the (100) face] multiplied by the value of this factor read for the appropriate glancing angle. Then, as before,  $A \sin \beta$  was plotted against  $\sin \beta$ .

The results are shown in fig. 2, and on comparing with fig. 1 it certainly seems that the general agreement has been improved. But further experiments are necessary before it can be definitely said whether this is significant.

The results have been re-analysed into the effects due to the Na and Cl atoms separately, using the sum and difference curves determined by the observed values corrected for "face effect" as in fig. 2, and the results differ from Bragg's by quantities up to 0.5 in  $F$ .

## § 7.3. Results for Sodium.

Table I. gives values of  $F$  calculated for several models of the sodium atom, for comparison with observed values. In all cases the dimensions of the orbit have been taken to be as calculated in the way already mentioned.

The atom models are :—

A. Spherically symmetrical atom,

(1)  $2\ 1_1$ ;  $4\ 2_1$ ;  $4\ 2_2$  orbits.

(2)  $1\ 1_1$ ;  $4\ 2_1$ ;  $5\ 2_2$  orbits.

(3)  $2\ 1_1$ ;  $2\ 2_1$ ;  $6\ 2_2$  orbits.

B. Atom with normals to planes of orbits fixed parallel to crystal axes.

C. Atom as defined in § 7.2, *i. e.* normals to planes of orbits making fixed angles  $\phi_0$  with the axis of the atom but capable of rotation round that axis; atom axes parallel to the three crystal axes and distributed equally among them.  $\sin^2 \phi_0 = 2/3$ .

For B and C the electron distribution is  $2\ 1_1$ ;  $4\ 2_1$ ;  $4\ 2_2$  orbits.

The entries for A are actual values of  $F$ , for the other models differences from A (1) are given. The “observed” values depend of course on the analysis of the experimental results into the effects of the two atoms separately. Values tabulated as “obs. 1” are taken from Bragg’s paper, those given as “obs. 2” are obtained from the results corrected for the “face effect” as described in the previous section. They are not given for the smallest glancing angle, as here the exact method of correcting for extinction is important and the results might not be comparable with Bragg’s. The observed values should be compared with the theoretical values in the row A (1), as there is little doubt that the electron distribution there assumed is correct.

TABLE I.  
Values of  $F$  or  $F_{\alpha\beta\gamma} - F_0$ .

Crystal face.		$\sin \beta = 0.1$ $0.2$ $0.3$ $0.4$ $0.5$					
Obs. (1).		8.32	5.40	3.37	2.02	0.76	
Obs. (2).			5.76	3.84	2.03	0.82	
Atom Model.	A (1).		8.87	6.18	3.41	1.66	1.18
	A (2).		8.76	5.81	2.70	0.66	0.04
	A (3).		9.01	6.58	3.79	1.70	0.78
	B [difference from A (1)]	100	-0.01	-0.15	-0.35	-0.83	-1.01
		111	0.01	0.21	0.45	1.02	1.61
	C [difference from A (1)]	100	-0.01	-0.08	-0.30	-0.60	-0.81
		311	0.00	-0.03	-0.09	-0.20	-0.27
		110	0.00	0.00	0.05	0.12	0.15
		111	0.00	0.05	0.21	0.45	0.68

It is very noticeable that the atom model with orbits in fixed planes gives larger differences between faces than atom C. This is to be expected since atom C gives an average distribution of charge more nearly uniform over a sphere than atom B, but the differences between atom C and the spherical atom are still very appreciable. The result A (1), (2), (3), shows that if the dimensions of the orbits are assumed, the results, for large glancing angles especially, are rather sensitive to the distribution of electrons among the orbits, but this distribution can probably be taken now as almost certain, and the experimental results looked on as possibly giving information about the dimensions of the orbits rather than about the electron distribution among them. Considering the many uncertainties, the agreement between theory and experiment for the orbital dimensions used does not seem at all bad.

#### § 7.4. Results for Chlorine.

Table II. gives the results for chlorine in the same general form as Table I. gives those for sodium. For chlorine no results have been calculated for an atom model with planes of orbits fixed, as the results for sodium indicate that the difference between faces for such an atom would be too large, and also the model C is probably a better approximation. The values \* of  $F$  for the spherically symmetrical atom model A are only given for the distribution of electrons:— $2\ 1_1$ ;  $4\ 2_1$ ;  $4\ 2_2$ ;  $4\ 3_1$ ;  $4\ 3_2$ .

TABLE II.

		Crystal face.	$\sin \beta =$	F or $F_{a\beta\gamma} - F_0$				
			0.1	0.2	0.3	0.4	0.5	
		Obs. 1.	12.72	7.85	5.79	4.40	3.16	
		Obs. 2.		8.23	6.05	4.25	3.30	
Atom Model.	{	A.	13.96	8.99	7.88	7.03	5.37	
		C-A.	100	- 0.08	- 0.62	- 0.74	- 0.06	0.00
			311	- 0.01	- 0.16	- 0.23	- 0.20	
			110	0.00	0.12	0.11	0.01	0.05
			111	0.04	0.47	0.73	0.46	0.43

The difference between calculated and observed values is much greater than for sodium, the observed values being too small. The difference is much larger than the effect of

\* The irregular differences between the values of  $F$  in successive columns of the table is due to the small number of values of  $\sin \beta$  for which  $F$  is tabulated. The curve of  $F$  against  $\sin \beta$  is quite smooth.

allowing for the difference between faces, it seems to be bigger at large glancing angles than at small, and is greater than two units in some cases.

The contributions of the different orbits to the calculated value of  $F$  are interesting. They are shown in Table III.

TABLE III.

		Contribution to F.				
Orbit.	$\sin \beta=0.1$	0.2	0.3	0.4	0.5	
2 $1_1$ .....	2.00	2.00	1.99	1.97	1.94	
4 $2_1$ .....	3.83	3.36	2.67	1.86	1.13	
4 $2_2$ .....	3.91	3.68	3.32	2.84	2.27	
4 $3_1$ .....	1.76	-0.27	+0.20	+0.08	-0.03	
4 $3_2$ .....	2.46	0.22	-0.10	0.28	+0.06	
<hr/>						
Total.....	13.96	8.99	7.88	7.03	5.37	

The small contributions from the  $3_1$  and  $3_2$  orbits at large angles are very noticeable. This is connected with the large range of  $r$  which they cover. The contribution of any one orbit is  $\oint [(\sin \xi)/\xi] d\mathbf{r}$  where  $\xi = (4\pi r \sin \beta)/\lambda$ ; and if the orbit is sufficiently large and eccentric, then at large glancing angles the range of integration will include several maxima and minima of  $(\sin \xi)/\xi$ , and the greatest weight will be given to those of least numerical value (since  $d\mathbf{r}/dr$  increases nearly all the way from inside to outside of the atom), so the total contribution will be very small. As already mentioned, the dimensions of the outer parts of the orbits are the most uncertain points in the calculated dimensions of the Cl orbits, but fortunately this uncertainty affects  $F$  at large glancing angles only very little for the reason given, and the big difference in this region between theoretical and observed values cannot be ascribed to it.

Two possible explanations of the difference are suggested, viz. :—

(1) The frequencies of the electrons in  $1_1$  orbits in Cl are becoming appreciable compared with the frequency of the incident X-rays, and those electrons may be scattering less than a free electron on classical electrodynamics; if this were the case, the electrons in other  $k=1$  orbits would perhaps, in the inner part of the orbit, also contribute less than the calculated amount to the scattering. The effect would be much less in sodium, for which the frequency of the electron in the  $1_1$  orbit is less, and also there are fewer other  $k=1$  orbits. To avoid large powers of 10 the frequencies  $p$  divided by  $cR$  can be compared ( $c$ =velocity of light in vacuo,

4 C 2

R=Rydberg number) and the values are approximately as follows:

	$\nu/R$ or $p/cR$ .
X rays used (Rh $K_\alpha$ ) . . . . .	1500
Cl $1_1$ orbit . . . . .	500
Na $1_1$ orbit . . . . .	200

so that the frequency in the  $1_1$  orbits of Cl is about a third of the frequency of the incident X-rays.

(2) It is very possible that the simple form used for the correction for the heat motion is not correct. It may well be, for example, that the value of  $F$  for the two atoms should be multiplied separately by different "Debye factors" before adding or subtracting to obtain the effective value of  $F$  for the odd or even faces.

### § 7.5. Results for Potassium.

Values of  $F$  at various glancing angles have also been calculated for potassium. The principal object of this calculation was to estimate the intensity of the (111) reflexion from sylvine. Since the K and Cl ions contain the same number of electrons in orbits of roughly the same dimensions, the odd order reflexions from the (111) face must be very weak, as is well known; but since the orbits have not exactly the same dimensions it would not be expected that the intensity of this reflexion would be absolutely zero, and it appeared worth while to calculate its value and see what information could be obtained from an experimental measurement of it.

For the first order reflexion from the (111) face of sylvine the calculated values of  $F_K - F_{Cl}$  and  $F_K + F_{Cl}$  are about 0.95 and 31 respectively; the principal part of  $F_K - F_{Cl}$  is due to the difference between the outer parts of the  $3_1$  orbits in K and Cl, and it is rather sensitive to the difference of the maximum radii of these two orbits; as already mentioned (§ 7.4) the calculation of the orbits of the Cl ion is most uncertain just in this region, and the measurement of the (111) reflexion from sylvine would be very valuable in giving further information; the dimensions of the orbits of the K ion are more certain.

The ratio of the intensities of (111) and (100) reflexions with the above values of  $F$  is about 1:800; the ratio of the intensities of the (333) and (100) reflexions comes out to be 1:6000, and of the (555) and (100) about 1:10000.

A similar experiment on NaF would also be interesting.

### § 8. Concluding Remarks.

In all the formulæ for  $F$  given in this paper, the actual dimensions of the atom only appear in the quantity

$\xi = (4\pi r \sin \beta)/\lambda$ , independent of the precise atom model used. Now for the reflexion at glancing angle  $\beta$ ,  $\lambda$  and  $\beta$  are connected by the Bragg relation,

$$2\pi d \sin \beta = n\lambda,$$

where  $d$  is the distance between successive reflecting planes in the crystal, so that  $F$  must be thought of not as a function of  $\lambda$  and  $\beta$  separately, but of  $(\sin \beta)/\lambda$ , or of  $n/d$ ; *i.e.* for a given crystal  $F$  is a function of the face from which reflexion takes place, and of the order of reflexion only, independent of the wave-length of the X-rays used\*.

This means that no new points on the curve of  $F$  against  $(\sin \beta)/\lambda$  can be obtained by using different values of  $\lambda$  so long as the same crystal is always used, but by using a different kind of crystal a different set of values of  $(\sin \beta)/\lambda$  are made available, and more points on the curve can be obtained.

It is fairly obvious from the arguments of § 3 that the X-ray reflexion from crystals can give us no evidence of the relative orientations of different orbits or relative phases of electrons in different orbits. This is because for an electron in a given position with respect to the nucleus, the contribution is the same whatever atom it belongs to, on account of the phase relations between the waves scattered by each atom as a whole. But when the centres of the scattering atoms are distributed at random in space, so that the intensities and not the amplitudes of the waves scattered by the various atoms have to be added, the phase differences between the wavelets scattered by the individual electrons in a single atom are important†. The intensity scattered by an amorphous mass (or by a crystal at an angle which is not a glancing angle for reflexion from a particular face) will therefore depend on the relative orientations of the orbits and phases of the electrons in a single atom, and it is just possible that some information on these points could be obtained from experimental data of X-ray scattering by amorphous substances (possibly solutions). But the theoretical formulæ for  $F$  are rather heavy, and numerical evaluation of  $F$  for any definite atomic model would involve the evaluation of several lengthy double integrals, and until better agreement between theory and experiment has been obtained for reflexion from crystals it does not seem probable that any valuable information could be obtained from amorphous materials.

\* This has already been mentioned incidentally by W. L. Bragg in a letter to 'Nature' (vol. ex. p. 148). He has also pointed out to me that the same is true of the Debye effect.

† W. L. Bragg has drawn attention to the difference between the effective value of  $F$  for an atom in a crystal and one in an amorphous mass of material (see B. J. B. i. p. 335).

CXVII. *The Spontaneous Loss of Energy of a Spinning Rod according to the Relativity Theory.* By A. S. EDDINGTON, M.A., F.R.S., *Plumian Professor of Astronomy in the University of Cambridge* \*.

A SPINNING rod sets up gravitational waves in the surrounding space, and the interesting question arises whether these waves will carry away the energy of rotation of the rod and gradually bring it to rest. This problem was first solved by Einstein †. An unimportant numerical slip in Einstein's result is corrected in a discussion by the author ‡, which for the most part followed similar methods. It appears that a rod of moment of inertia  $I$  with angular velocity  $\omega$  will lose energy per unit time at the rate

$$\frac{32}{5} k I^2 \omega^6,$$

where  $k=1$  if the units are such that the constant of gravitation and the velocity of light are unity, and  $k=2.7 \cdot 10^{-60}$  for C.G.S. units. In all practical cases the loss is extremely small.

On account of the picturesque interest of the problem it may be desirable to give a deduction of this result by a totally different method, which is considerably shorter than the discussions above quoted. In this method we pay no attention to the waves receding into the distance, which by an analytical fiction are supposed to bear the energy away. (The waves are real enough, but their pseudo-energy-tensor is not regarded in the relativity theory as real energy.) The loss of energy is considered from another aspect which has a certain historic interest. If gravitation is not propagated instantaneously the lag may introduce tangential components of the force opposing the motion of the system. This was the effect looked for by Laplace when he considered a finite velocity of propagation of gravitation in astronomical systems; from its non-appearance he deduced that the speed must be very much greater than that of light. Modern theory shows that the first order effect looked for by Laplace (proportional to  $v^2/c^2$ ) is eliminated; but the result here found is actually the residual Laplace effect of the third order (proportional to  $v^6/c^6$ ). The mutual attraction of the particles of the rod is, owing to the rotation, not exactly in the instantaneous line of the rod, and the resultant is a couple which slowly

\* Communicated by the Author.

† Berlin *Sitzungsberichte*, 1916, p. 688; 1918, p. 154.

‡ Proc. Roy. Soc. 102 A. p. 268 (1922).

destroys the rotation. It will, however, be explained in due course that the present result does not solve Laplace's problem for an astronomical system, but is limited to cohesive systems.

From the well-known equation \*

$$\partial \mathfrak{T}_\mu^\nu / \partial x_\nu = \frac{1}{2} \mathfrak{T}^{\alpha\beta} \partial g_{\alpha\beta} / \partial x_\mu,$$

we have for  $\mu=4$

$$\frac{\partial \mathfrak{T}_4^\nu}{\partial x_\nu} = \frac{1}{2} \mathfrak{T}^{\alpha\beta} \frac{\partial g_{\alpha\beta}}{\partial t}.$$

Hence, integrating over a three-dimensional region enclosing the spinning rod,

$$\frac{\partial}{\partial t} \int \mathfrak{T}_4^\nu dV = \frac{1}{2} \int \mathfrak{T}^{\alpha\beta} \frac{\partial g_{\alpha\beta}}{\partial t} dV, \quad . \quad . \quad . \quad (1)$$

since the other terms on the left give surface integrals which vanish because the boundary does not pass through matter. Equation (1) expresses the rate of change of material energy in the region, *i. e.* in the rod which is the only material system there.

In calculating approximate values of  $\partial g_{\alpha\beta} / \partial t$  we shall find it necessary to retain rather high powers of the velocities in the coefficients of periodic terms. But the same accuracy is not needed for steady factors such as  $\sqrt{-g}$  or  $(1-v^2)^{-\frac{1}{2}}$  which merely multiply the final result; these will be set equal to unity and  $T^{\alpha\beta}$  may thus be substituted for  $\mathfrak{T}^{\alpha\beta}$ .

We write  $g_{\alpha\beta} = \delta_{\alpha\beta} + h_{\alpha\beta}$  where  $\delta_{\alpha\beta}$  denotes the Galilean values, and the square of the small disturbance  $h_{\alpha\beta}$  is neglected. Then, as Einstein has shown, the law of gravitation will be satisfied by

$$\square h_{\alpha\beta} = 2G_{\alpha\beta} = -16\pi(T_{\alpha\beta} - \frac{1}{2}\delta_{\alpha\beta}T). \quad . \quad . \quad . \quad (2)$$

This is the ordinary wave-equation of which the solution is given by an integral taken over the properly antedated strengths and positions of the sources, *viz.*

$$h_{\alpha\beta} = -4 \int \left[ \frac{T'_{\alpha\beta} - \frac{1}{2}\delta_{\alpha\beta}T'}{r(1-v_r)} \right] dV'. \quad . \quad . \quad . \quad (3)$$

The square bracket indicates antedated values;  $r$  is the distance from  $dV'$  at the appropriate moment to the point where  $h_{\alpha\beta}$  is to be calculated;  $v_r$  is the component velocity

\* For this equation and (2) and (3) see (55·6), (57·7), and (74·71) in my 'Mathematical Theory of Relativity.' They are standard formulæ which will be found in most treatises.



of  $dV'$  towards this point. The necessity for the factor  $(1-r_r)$  was pointed out by Liénard and Wiechert.

By (1) and (3) the rate of loss of energy of the rod is

$$2 \iint \left\{ T^{\alpha\beta} \frac{\partial}{\partial t} \left[ \frac{T'_{\alpha\beta}}{r(1-r_r)} \right] - \frac{1}{2} T \frac{\partial}{\partial t} \left[ \frac{T}{r(1-r_r)} \right] \right\} dV dV' \quad (4)$$

since  $T^{\alpha\beta} \delta_{\alpha\beta} = T$ . It will be seen that in this integral the loss is exhibited as arising from the mutual action of pairs of elements of the rod,  $dV$  and  $dV'$ .

The square brackets can be expanded in terms of contemporaneous values of  $r$  and  $T'_{\alpha\beta}$  by the series\*

$$\left[ \frac{T'_{\alpha\beta}}{r(1-r_r)} \right] = \frac{T'_{\alpha\beta}}{r} - \frac{d}{dt} T'_{\alpha\beta} + \frac{\sum}{2} \frac{(-)^n}{n!} \frac{d^n}{dt^n} (r^{n-1} T'_{\alpha\beta}), \quad (5)$$

the quantities on the right *not* being antedated.

Let the rod, spinning in the  $xy$ -plane, be along the axis of  $x$  at the instant  $t=0$ , the origin being at the centre. Let the element  $dV$  then be at  $x$  and  $dV'$  at  $x'$ . The varying distance of the element  $dV'$  from the fixed point  $x$  instantaneously occupied by  $dV$ , is

$$r = (x^2 + x'^2 - 2xx' \cos \omega t)^{1/2}.$$

This must be used in (5), and  $t$  must be made zero after the differentiations. For the present application we can simplify (5) by noting that if  $T^{\alpha\beta}$  is a component which does not vanish for  $t=0$ ,  $T'_{\alpha\beta}$  will be an even function of  $t$ , so that derivatives of odd order disappear. Accordingly

$$\begin{aligned} \frac{\partial}{\partial t} \left[ \frac{T'_{\alpha\beta}}{r(1-r_r)} \right] &= - \frac{d^3}{dt^3} T'_{\alpha\beta} - \frac{1}{6} \frac{d^4}{dt^4} \{ T'_{\alpha\beta} (x^2 + x'^2 - 2xx' \cos \omega t) \} \\ &\quad - \frac{1}{120} \frac{d^6}{dt^6} \{ T'_{\alpha\beta} (x^2 + x'^2 - 2xx' \cos \omega t)^2 \} - \dots \quad (6) \end{aligned}$$

We have then to substitute (6) in (4) and pick out the earliest non-vanishing terms. Note that terms containing an odd power of  $x$  or  $x'$  will vanish on integration along the rod, assuming it to be symmetrical.

(a) *Stress components,  $T^{11}$ ,  $T^{22}$ .*

For these only the first term of (6) is required, and since  $r$  is then not involved the double integration breaks up into the product of two independent integrals. The loss of energy is

$$-2 \int T^{11} dV \cdot \frac{d^2}{dt^2} \int T'_{11} dV' - 2 \int T^{22} dV \cdot \frac{d^2}{dt^2} \int T'_{22} dV'. \quad (7)$$

\* I am not sure if this expansion is published elsewhere; a proof is given at the end of this paper.

If  $\sigma$  is the line-density of the rod,  $T^{22}dV = \sigma\omega^2 x^2 dx$ . Hence

$$\int T^{22}dV = I\omega^2.$$

The component  $T^{11}$  represents the tension in the rod and it is easily found from elementary dynamics that its integral is  $-I\omega^2$ .

For the moving element the corresponding integrals are  $I\omega^3 \cos 2\omega t$  and  $-I\omega^2 \cos 2\omega t$ . Hence (7) gives the result  $16 I^2 \omega^6$ .

(b) *Momentum components,  $T^{24}$ ,  $T^{42}$ .*

$$T^{24}dV = \sigma\omega x dx, \quad T'_{24}dV' = -\sigma'\omega x' dx' \cos \omega t.$$

The first term of (6) now yields nothing owing to the odd powers of  $x$  and  $x'$ . We take the second term and obtain

$$-2 \iint \sigma\omega x dx \cdot \sigma'\omega x' dx' \cdot \frac{1}{6} (2\omega)^4 x x' = -\frac{16}{3} I^2 \omega^6.$$

$T^{42}$  gives an equal contribution, making a total of  $-\frac{32}{3} I^2 \omega^6$ .

(c) *Mass components,  $T^{44}$ ,  $T$ .*

$$T^{44}dV = \sigma dx, \quad T'_{44}dV' = \sigma' dx'.$$

The third term of (6) is now needed, giving

$$2 \iint \sigma dx \cdot \sigma' dx' \cdot \frac{1}{120} (2\omega)^6 \cdot 2x^2 x'^2 = \frac{32}{15} I^2 \omega^6.$$

The proper-density  $T$  and the coordinate-density  $T^{44}$  are practically the same, so that the term in  $T$  takes away again half the above amount leaving  $\frac{16}{15} I^2 \omega^6$ .

Gathering together (a), (b), and (c) the rate of loss of energy is

$$\left(16 - \frac{32}{3} + \frac{16}{15}\right) I^2 \omega^6 = \frac{32}{5} I^2 \omega^6, \quad \dots \quad (8)$$

agreeing with the result already stated.

If  $a$  is of the order of magnitude of the linear dimensions of the rod, and  $v$  the linear velocity, the result (8) is of order  $(M/a)^2 v^6$ . Since we have neglected higher powers of the gravitational potential, terms of order  $(M/a)^3 v^2$  or  $(M/a)^4 v^2$  have not been investigated. The result is only valid if these are small compared with (8). For a spinning rod there is no theoretical difficulty in constructing examples in which

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this condition is satisfied ; but in a double star system \*  $r^2$  is necessarily of the same order of magnitude as  $\dot{M}/\alpha$ , so that the approximation is *never* permissible.

*Series expansion of Retarded Potentials.*

The expansion (5) is obtained as follows. Consider a fixed point P at the instant  $t$  and a moving source P' at the instant  $t - \tau$ . Let the distance PP' be given as a function of the time so that

$$PP' = r = f(t - \tau).$$

Then the component velocity of P' along P'P is

$$v_r = -dr/dt = -f'(t - \tau).$$

Suppose that the wave emitted from P' at the time  $t - \tau$  has at the time  $t$  reached the point Q in the direction P'P. Let  $PQ = \alpha$ , so that

$$\alpha = \tau - r = \tau - f(t - \tau), \quad \dots \dots (9)$$

the wave-velocity being unity.  $\alpha$  is then a function of  $\tau$ , and *vice versa*.

By differentiation

$$1 = \frac{d\tau}{d\alpha} + f'(t - \tau) \frac{d\tau}{d\alpha} = \frac{d\tau}{d\alpha} (1 - v_r).$$

Hence if  $\phi(t - \tau)$  is any quantity associated with the source at P' at the time  $t - \tau$ ,

$$\left\{ \frac{\phi}{r(1 - v_r)} \right\}_{t-\tau} = \frac{\phi(t - \tau)}{f(t - \tau)} \frac{d\tau}{d\alpha} = \frac{d}{d\alpha} F(t - \tau),$$

where

$$F' = -\phi/f. \quad \dots \dots (10)$$

The appropriate moment required for calculating a retarded potential is obtained by putting  $PQ = \alpha = 0$ . Hence

$$\left[ \frac{\phi}{r(1 - v_r)} \right] = \left\{ \frac{d}{d\alpha} F(t - \tau) \right\}_{\alpha=0} \quad \dots (11)$$

By Lagrange's theorem on the expansion of an implicit function which by (9) satisfies

$$(t - \tau) = (t - \alpha) - f(t - \tau)$$

\* The density of the rod is not assumed to be uniform, so that at first sight a double star would appear to be simply a particular case of a rod.

we have

$$\begin{aligned} F(t-\tau) &= F(t-\alpha) - F'(t-\alpha)f(t-\alpha) \\ &\quad - \sum_2^{\infty} \frac{1}{n!} \frac{\partial^{n-1}}{\partial \alpha^{n-1}} [F'(t-\alpha)\{f(t-\alpha)\}^n] \\ &= F(t-\alpha) + \phi(t-\alpha) \\ &\quad + \sum_2^{\infty} \frac{1}{n!} \frac{\partial^{n-1}}{\partial \alpha^{n-1}} [\phi(t-\alpha)\{f(t-\alpha)\}^{n-1}]. \end{aligned}$$

Hence

$$\begin{aligned} \frac{d}{d\alpha} F(t-\tau) &= \frac{\phi(t-\alpha)}{f(t-\alpha)} - \phi'(t-\alpha) \\ &\quad + \sum_2^{\infty} \frac{1}{n!} \frac{\partial^n}{\partial \alpha^n} [\phi(t-\alpha)\{f(t-\alpha)\}^{n-1}]. \end{aligned}$$

Substituting in (11) and noticing that  $\partial/\partial\alpha = -\partial/\partial t$ ,

$$\left[ \frac{\phi}{r(1-r_r)} \right] = \frac{\phi}{r} - \frac{d\phi}{dt} + \sum_2^{\infty} \frac{(-)^n}{n!} \frac{d^n}{dt^n} (r^{n-1}\phi), \quad (12)$$

where on the right  $\phi$  and  $r$  are to be taken for the time  $t$ .

This result is available for calculating electromagnetic potentials irrespective of the theory of relativity as well as for the gravitational potentials in (5).

## CXVIII. The Sparking-potential of Gases.

By G. HOLST and E. OOSTERHUIS\*.

1. **I**N his paper "Ionization by Collision"† J. S. Townsend has discussed a theory of the sparking-potential of gases suggested by us in a short note in the *Comptes Rendus*‡. This theory is based on the assumption that positive ions can liberate electrons from the cathode, no ionization taking place by the collision of a positive ion against a gas molecule. It may be of interest to give here an account of the considerations and experimental facts underlying this hypothesis.

2. A gas molecule can be ionized by an electron as soon as the energy of the electron reaches a certain value corresponding to the ionization-potential of the molecule. In order that a positive ion may be able to ionize, it should have *at least* the same energy. In many cases the conditions in a discharge-tube are such that it is impossible for a positive ion to acquire this energy.

\* Communicated by the Authors.

† J. S. Townsend, *Phil. Mag.* vol. xlv, p. 444 (March 1923).

‡ G. Holst and E. Oosterhuis, *C. R.* t. clxxv, p. 577 (1922).

From Gill and Pidduck's measurements\* in helium we take the following data: for a pressure of 5 mm. and electrode distance 78 cm. a sparking-potential of 156 volts was found. The mean free path being only 0.03 mm., the voltage drop per mean free path in the direction of the field is 0.6 volt. Now the ionization potential of helium amounts to about 25 volts, so that the ion should describe a path *at least* 40 times greater than the average in the direction of the field in order to ionize. The probability of describing a path of this length in an arbitrary direction being already  $< 10^{-17}$ , it becomes evident that practically all ionization by positive ions can be neglected.

3. During a series of determinations of current-potential curves in argon and neon we had observed that in argon the probability that an electron loses its energy at a velocity below that corresponding to the ionizing potential is much larger than in the case of neon †.

Later experiments with neon have shown that in all cases where the number of collisions is not very large, practically all the electrons will ionize without losing part of their energy by excitation in a preceding collision. Ionization itself seems to be readily produced. It could therefore be expected that the phenomena in neon would show a very simple character, and for this reason most of our experiments and considerations relate to neon.

4. If an electric current passes through a tube filled with neon a glow can already be observed at very small currents of the order of magnitude of  $10^{-9}$  amp. The appearance of this glow can give us some information about the phenomena going on during the discharge.

A neon discharge-tube with electrode distance about 1 cm., gas pressure about 1 cm., was put in series with a diode. By regulating the filament current of the latter, the current in the neon tube could be varied from very small values to a value where the cathode glow begins. So the successive forms of the discharge were studied. First a very dull glow near the anode is observed. On increasing the current a series of black and luminous layers appears, a perfectly black one just in front of the cathode followed by a very sharply limited luminous layer, etc.; the layers becoming more diffuse near the anode. At higher current this striated form

\* (cf. J. S. Townsend, 'Electricity in Gases,' p. 325 (1915).

† G. Holst and E. Oosterhuis, *Physica*, i. p. 80 (1921); cf. also H. C. Rentschler, *Phys. Rev.* (2) xiv. p. 503 (1919).

of discharge makes place for the ordinary cathode glow ; the first black layer near the cathode persists, however \*.

The fact that six or seven layers can easily be observed points out that practically all the electrons must lose their energy at the same distance from the cathode. The number of layers is equal to the potential on the tube divided by the ionizing potential. The appearance of these layers is the main basis of our hypothesis that the electrons are liberated at the cathode surface. If they were generated in the bulk of the gas it would be very difficult to explain these partly perfectly sharp layers.

Now the sparking-potential may be defined as the potential which is required to maintain a very small current †, so that we may expect that the mechanism of the sparking is analogous to that observed with small currents : the electrons liberated from the cathode ionize at definite distances from the latter.

5. In experiments with discharge-tubes containing two electrodes of different material we found ‡ that the minimum sparking-potential in neon can vary as 1:3, depending on the material of the cathode. The lowest value was found using rubidium or caesium as cathode, the highest value was observed with a carbon cathode. If we now consider the minimum sparking-potential for different gases, the cathode being of the same metal, we find that the minimum sparking-potentials also vary about as 1:3 §. It follows that the minimum sparking-potential depends as much on the nature of the cathode material as it does on the nature of the gas.

6. The facts described above lead us to consider a hypothetical ideal gas, in which :

- (1) An electron loses no energy whatsoever in collisions as long as its velocity is below that corresponding to the ionizing potential.
- (2) An electron will ionize as soon as its velocity is equal to the ionization potential  $V_i$ .
- (3)  $n$  positive ions will liberate one electron at the cathode surface.
- (4) No positive ion ionizes a gas molecule by collision.

\* G. Holst and E. Oosterhuis, *Physica*, i, p. 86 (1921): cf. F. W. Aston, *Proc. Roy. Soc. (A)* lxxx, p. 45 (1908).

† J. S. Townsend, 'Electricity in Gases,' p. 430 (1915).

‡ G. Holst and E. Oosterhuis, *Versl. Kon. Ak. v. Wet. Amsterdam*, xxix, p. 849 (1920).

§ J. S. Townsend, 'Electricity in Gases,' p. 529 (1915).

An electron starts at the cathode. At a distance  $d$  from the cathode—where the electron has fallen through a P.D. equal to  $V_i$ —it ionizes for the first time, forming one new electron and one positive ion. At a distance  $2d$  it ionizes again, and so on. The total number of positive ions formed is  $2^g - 1$ ,  $g$  being the number of times the process is repeated.

Sparking will occur when these ions, on reaching the cathode, liberate one electron or more, for in that case the current will continue to flow. As soon as  $g$  reaches a value  $g_s$ , given by the relation  $2^{g_s} - 1 > n$ , the condition for sparking is reached; the sparking-potential  $V_s$  is equal to  $g_s V_i$ .\*

$n$  will be different for different cathode materials and for different ions.  $n$  will be larger if it is difficult to extract an electron from the cathode, and thus  $n$  will depend on  $\phi$ , the work necessary to liberate an electron from the cathode. Indeed, we have shown that there is a parallelism between the sparking-potential for different cathode materials and Richardson's constant  $\phi$ †.

For our hypothetical ideal gas the sparking-potential  $V_s = g_s V_i$  would be independent of the gas pressure and the electrode distance; it depends only on the ionization potential of the gas and on the number of electrons liberated from the cathode by a positive ion.

7. Our ideal gas is only a rough first approximation. In a real gas the sparking-potential depends on gas pressure and electrode distance. This is due to the fact that in a real gas energy is lost by collisions.

We now consider a second approximation. The energy loss is limited to the loss  $\Delta E = 2 \frac{m}{M} E$  which the electron of mass  $m$  and energy  $E$  suffers in an elastic collision against a gas molecule of the mass  $M$ , all other energy losses being neglected as long as the velocity of the electron is smaller than that corresponding to the ionization potential.

We then find:

$$V_s = V_i \frac{273 a p \sqrt{2k}}{T \cdot 76 \cdot \lambda_n \sqrt{2}} \frac{e^{\frac{273 a p \sqrt{2k}}{T \cdot 76 \cdot \lambda_n \sqrt{2}} + 1}}{e^{\frac{273 a p \sqrt{2k}}{T \cdot 76 \cdot \lambda_n \sqrt{2}} - 1}},$$

\* On this theory the sparking-potential is a multiple of  $V_i$ , if different cathode materials are used. Our experiments point in this direction. Compare also H. Schüller, *Phys. Zs.* xxiv. p. 259 (1923).

† G. Holst and E. Oosterhuis, *Physica*, i. p. 84 (1921).

in which

$a$  = electrode distance (cm.);

$p$  = gas pressure (cm. Hg);

$\lambda_n$  = mean free path of a molecule of the gas at 0° C. and 76 cm. ;

$$k = 2 \frac{m}{M}.$$

The formula shows that the sparking-potential is a function of  $ap$  (Paschen's law). It holds approximately for neon near the minimum sparking-potential\*. It does not hold for argon. This is to be expected, because in argon the probability of an energy loss in an exciting collision (at voltages over 12 volts) is very much larger than in neon. These energy losses may not be neglected here. In the case of argon a further approximation would be necessary to find  $V_s$  as a function of  $a, p$ , and  $g_s$ . If  $V_1$  is the lowest potential at which an excitation can take place,  $V_2$  the second, and so on,  $\eta_1$  the probability that an electron loses the energy  $eV_1$ ,  $\eta_2$  the probability to lose  $eV_2$  and so on, the average energy loss will be

$$\eta_1 n_1 V_1 e + \eta_2 n_2 V_2 e + \dots,$$

where  $n_1$  is the number of collisions between  $V_1$  and  $V_2$ ,  $n_2$  between  $V_2$  and  $V_3$ , and so on. The probabilities  $\eta_1 \dots$  have not yet been determined. Moreover, the calculation of the number of collisions in argon is very difficult, as the apparent diameter of the molecule, according to Ramsauer†, is not a constant. So, even in the case of argon, no formula for  $V_s$  can be derived.

With helium a new complication is introduced by the fact that metastable states appear.

In the case of polyatomic gases new difficulties arise due to inelastic collisions and electron affinity.

The departure from the ideal gas is due to energy losses of the electrons. If the number of collisions is small these losses will be less important. That is the reason why the minimum sparking-potentials for gases are not very far apart, the difference in sparking-potential increasing with pressure and electrode distance.

\* We must point out that these considerations apply only to gas pressures  $p$  and electrode distances  $a$  larger than those corresponding to the minimum sparking-potential. For smaller values of  $pa$  the number of collisions becomes too low, so that the sparking-potential increases.

† C. Ramsauer, *Phys. Zeitschr.* xxii. p. 613 (1921); G. Hertz, *Proc. Amsterdam*, xxv. nos. 3 & 4 (1922).



8. There is one point in our reasoning that must be considered somewhat more in detail. Our experiments showed us that the probability that excitation occurs in neon is very small. On the other hand, the *luminous* layers observed with small currents show that not only ionization occurs but also some excitation. The sharpness of the layers proves, however, that the number of collisions giving excitation is small compared with the number of ionizing collisions. This is in accordance with the fact that the amount of light per unit of current given out by the luminous layers is very much smaller than in the positive column.

Physical Laboratory,  
Philips' Incandescent Lamp Works,  
Eindhoven.

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### CXIX. *Notices respecting New Books.*

*The Structure of the Atom.* By E. N. DA C. ANDRADE, D.Sc., Ph.D.  
(G. Bell & Co.) 16s.

ATOMIC Physics has been developing recently at such a great rate that those general students of science who have been unable to keep pace with the literature will heartily welcome Professor E. N. da C. Andrade's book entitled 'The Structure of the Atom.'

In a volume of only 300 pages it is hardly to be expected that a comprehensive survey of this vast subject in all its details should have been made, but the author has succeeded in so small compass in giving quite a good general survey. Its utility to the reader is enhanced by the addition at the end of each chapter of references to some of the more important original published memoirs.

The book is divided into two sections, the first dealing with the nucleus, and the second treating the structure outside the nucleus.

It naturally follows, therefore, that the eight chapters under the first heading are devoted in the main to a consideration of Radioactivity and Positive Rays, while the remaining six chapters deal with the various dynamic and static models of the atom which have been proposed in recent years and their success in correlating the known experimental data in X-rays, spectroscopy, and chemistry, and in suggesting new lines for experimental and theoretical investigations.

We sincerely congratulate the author on his very useful work and hope that another volume may soon appear.

Published by G. Bell, the book is excellently produced, easy to read, and well illustrated.

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